



1 **Intense  $p\text{CO}_2$  and  $[\text{O}_2]$  Oscillations in a Mussel-Seagrass Habitat:**  
2 **Implications for Calcification.**

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4 **Vincent Saderne<sup>1,2</sup>, Peer Fietzek<sup>1,3</sup>, Jens Daniel. Müller<sup>4</sup>, Arne Körtzinger<sup>1,5</sup> and**  
5 **Claas Hiebenthal<sup>1</sup>**

6 [1]{GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany}

7 [2]{KAUST King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi  
8 Arabia}

9 [3]{Kongsberg Maritime Contros GmbH, Kiel, Germany}

10 [4]{Leibniz Institute for Baltic Sea Research, Warnemünde, Germany}

11 [5]{Christian Albrecht University, Kiel, Germany}

12 Correspondence to: V. Saderne ([vincent.saderne@KAUST.edu.sa](mailto:vincent.saderne@KAUST.edu.sa))

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14 **Abstract**

15 Numerous studies have been conducted on the effect of ocean acidification on calcifiers inhabiting  
16 nearshore benthic habitats, such as the blue mussel *Mytilus edulis*. The majority of these  
17 experiments was performed under stable  $\text{CO}_2$  partial pressure ( $p\text{CO}_2$ ), carbonate chemistry and  
18 oxygen ( $\text{O}_2$ ) levels, reflecting present or expected future open ocean conditions. Consequently,  
19 levels and variations occurring in coastal habitats, due to biotic and abiotic processes, were mostly  
20 neglected, even though these variations largely override global long-term trends. To highlight this  
21 hiatus and guide future research, state-of-the-art technologies were deployed to obtain high-  
22 resolution time series of  $p\text{CO}_2$  and  $[\text{O}_2]$  on a mussel patch within a *Zostera marina* seagrass bed,  
23 in Kiel Bay (western Baltic Sea) in August and September 2013. Combining the in situ data with  
24 results of discrete sample measurements, a full seawater carbonate chemistry was derived using  
25 statistical models. An average  $p\text{CO}_2$  more than 50% ( $\sim 640 \mu\text{atm}$ ) higher than current atmospheric  
26 levels was found right above the mussel patch. Diel amplitudes of  $p\text{CO}_2$  were large:  $765 \pm 310$   
27 (mean  $\pm$  SD). Corrosive conditions for calcium carbonates ( $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}} < 1$ ) centered on sunrise



28 were found, but the investigated habitat never experienced hypoxia throughout the study period. It  
29 is estimated that mussels experience conditions limiting calcification for 12 - 15 h per day, based  
30 on a regional calcium carbonate concentration physiological threshold. Our findings call for more  
31 extensive experiments on the impact of fluctuating corrosive conditions on mussels. We also stress  
32 the complexity of the interpretation of carbonate chemistry time series data in such dynamic coastal  
33 environments.

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## 36 **1 Introduction**

37 Since preindustrial times, the atmospheric CO<sub>2</sub> mixing ratio rose from approximately 280 ppmv  
38 to actual ~400 ppm (Mauna Loa, annual mean 2016, NOAA-ESRL). Future climate scenarios  
39 predict a strong further increase of up to 1000 ppm by the year 2100 (IPCC, 2013). The dissolution  
40 of anthropogenic CO<sub>2</sub> in seawater causes an increase in the seawater CO<sub>2</sub> partial pressure (*p*CO<sub>2</sub>)  
41 and a concurrent decrease of the seawater pH, a global phenomenon also referred to as ocean  
42 acidification (OA) (Bates et al., 2014 and Doney et al., 2009).

43 OA reduces the supersaturation of seawater with respect to calcite and aragonite, which may cause  
44 seawater to become corrosive for these calcium carbonates, that compose the shells and skeletons  
45 of marine species (see Harvey et al., 2013 and Andersson et al., 2011 for review and meta-  
46 analysis). In their review, Wahl et al. (2015) counted a total of 350 studies on the response of  
47 benthic marine fauna and flora to ocean acidification, either in the field or in mesocosms. The  
48 majority of these studies considered open ocean pH and *p*CO<sub>2</sub> as reference for the scenarios  
49 employed to study the impact of OA. Indeed, the carbonate system (pH, *p*CO<sub>2</sub>, dissolved inorganic  
50 carbon (DIC) and total alkalinity (TA)) in surface oceans is understood relatively well, and many  
51 models exist predicting the future rise of *p*CO<sub>2</sub> and decrease of pH (e.g. Orr et al., 2005). However,  
52 very recent articles highlight the inapplicability of these predictions for the nearshore environment  
53 (Duarte et al., 2013; Wahl et al., 2015; Müller et al., 2016) and the serious lack of relevant datasets  
54 for the different major types of benthic habitats worldwide (Wahl et al., 2015). In addition to OA,  
55 ocean warming and eutrophication of coastal waters around the world cause a spreading and  
56 shoaling of hypoxia ([O<sub>2</sub>] < 60 μmol kg<sup>-1</sup>) in the ocean's interior (Diaz and Rosenberg, 2008;  
57 Keeling et al., 2010).



58 In nearshore areas, metabolic processes by flora and fauna (photosynthesis, respiration and  
59 calcification) and redox reactions in the sediment (e.g. sulfate reduction/sulfide oxidation,  
60 denitrification/nitrification) strongly affect the carbonate chemistry of the water column,  
61 temporarily generating strong disequilibria for CO<sub>2</sub> and O<sub>2</sub> between the sea and the atmosphere.  
62 Cycles of super- and undersaturation for these two metabolic gases have been observed in all kinds  
63 of benthic habitats at daily and seasonal scale, but also in relation to physical forcing such as tides,  
64 wind or precipitation (Hofmann et al., 2011; Saderne et al., 2013; see Wahl et al., 2015 for review).

65 As an example, in the western Baltic Sea (Eckernförde Bay) Saderne et al. (2013) found daily  
66 variations of *p*CO<sub>2</sub> of 200 - 400 μatm between July and September in a macrophyte meadow  
67 dominated by the brown algae *Fucus serratus*, with maximum *p*CO<sub>2</sub> levels reaching up to  
68 approximately 2200 μatm during upwelling conditions. As a consequence, seawater saturation  
69 states for calcite and aragonite ( $\Omega_{\text{calc}}$  and  $\Omega_{\text{arag}}$ ) repeatedly fell below the dissolution threshold ( $\Omega$   
70  $< 1$ , i.e. seawater turning undersaturated and hence corrosive to these biominerals) during the  
71 upwelling event, which was monitored over several days.

72 Here, we present a case study of a mixed seagrass/mussel bed, illustrating the carbonate chemistry  
73 conditions typically experienced by calcifiers in their natural habitat. We measured *p*CO<sub>2</sub> and  
74 dissolved oxygen ([O<sub>2</sub>]) directly above a mussel patch of less than 2 m<sup>2</sup> extension, surrounded by  
75 seagrass, in a mosaic seagrass-mussel habitat as it is characteristic for western Baltic Sea nearshore  
76 benthic habitats. We used a combination of autonomous in situ sensors for *p*CO<sub>2</sub>, [O<sub>2</sub>], salinity  
77 and temperature, complemented by discrete sampling for DIC, TA, phosphate, and silicate, for a  
78 period of more than 7 weeks in summer 2013. Using statistical modeling, we derived time series  
79 for the entire study period for carbonate chemistry parameters including  $\Omega_{\text{calc}}$  and  $\Omega_{\text{arag}}$ . Based on  
80 literature knowledge regarding effects of carbonate ion concentration ([CO<sub>3</sub><sup>2-</sup>]) as well as  $\Omega_{\text{calc}}$  and  
81  $\Omega_{\text{arag}}$  effects on mussel biomineralization, we identified time windows of potentially favorable and  
82 unfavorable conditions for mussel calcification.

83

## 84 **2. Materials and Methods**

### 85 **2.1 Description of Kiel Bay and the experimental site**



86 Kiel Bay is a narrow and shallow bay in the western Baltic Sea that consists of two basins. The  
87 inner Kiel Bay (see Fig. 1A) in the south is up to approximately 2 km wide and (except for a few  
88 deeper dips) up to 14 m deep, while the outer Kiel Bay is up to approximately 5 km wide and  
89 approximately 20 m deep and opens in the north to the larger Kiel Bight (Kögler and Ulrich, 1985;  
90 Schwarzer and Themann, 2003). Surface and bottom water bodies of the larger Kiel Bight swash  
91 in and out Kiel Bay (mainly driven by varying wind directions and intensities). Freshwater influx  
92 from the small river “Schwentine” (east side of Kiel Bay, opposite to GEOMAR on Fig. 1A) also  
93 shapes the hydrology of the inner Kiel Bay. The strict separation of deep and shallow water bodies  
94 by stratification in the larger Kiel Bight and its bays that typically occurs during summer months  
95 is occasionally broken-up by wind-driven upwelling. The shallow coastal communities are then  
96 put in contact with high CO<sub>2</sub> and sometimes hypoxic sub-surface waters (Feely et al., 2008;  
97 Melzner et al., 2013).

98 In Kiel Bay, as in several other enclosed bays of the western Baltic Sea, the blue mussel *Mytilus*  
99 *edulis* and the seagrass *Zostera marina* co-occur in patches forming mosaic habitats (Reusch and  
100 Chapman, 1995; Vinther et al., 2008; Vinther and Holmer 2008; Vinther et al. 2012). A sensor  
101 package measuring pCO<sub>2</sub>, [O<sub>2</sub>], salinity and temperature was deployed at 2 m depth in a mixed  
102 habitat formed by *Z. marina* and *M. edulis* in Kiel Bay, western Baltic Sea (54.3467 °N,  
103 10.1539 °E; see Fig.1A). The package was directly placed on a mussel patch within the seagrass  
104 bed. The deployment was conducted for 50 days from the 08.08.2013 to 27.09.2013 with short  
105 power interruptions from 10.08., 17:10 to 11.08., 8:00 and from 12.08., 5:00 to 14.08., 16:00.

## 106 **2.2 In situ sensor suite**

107 Temperature, salinity and [O<sub>2</sub>] were measured simultaneously every 10 min with a SBE 37–SI  
108 MicroCAT (temperature and salinity, Sea-Bird Electronics Inc., USA) and an oxygen optode  
109 Aanderaa 3835 (Aanderaa Data Instruments AS, Norway) enclosed in a flow cell. The circulation  
110 of water between the SBE 37–SI and the optode was achieved by means of an SBE 5M pump  
111 (Sea-Bird Electronics Inc., USA) that ran for 30 seconds every 10 min. The coordination of  
112 pumping and recording by the SBE 37 and the optode was carried out by a custom-made data  
113 logger (Todd Martz Laboratory, Scripps Institution of Oceanography, San Diego, USA). To  
114 prevent fouling on sensors, the SBE 37–SI was equipped with tributyltin tablets and copper tubing  
115 linked the SBE 37–SI and the flow cell to the pump.



116 A HydroC<sup>®</sup> CO<sub>2</sub> II sensor (KM Contros GmbH, Kiel, Germany) was used to autonomously  
117 measure in situ CO<sub>2</sub> partial pressure (*p*CO<sub>2</sub>). The sensor determines *p*CO<sub>2</sub> optically by means of  
118 an nondispersive infrared (NDIR) absorption measurement within a membrane-equilibrated  
119 headspace (Fietzek et al., 2014). The sensor was calibrated at a water temperature of 17.5 °C at 6  
120 different *p*CO<sub>2</sub> levels across a measurements range of 200 - 2200 μatm by the manufacturer before  
121 (July) and after (November) the measurements. The corresponding calibration polynomials had a  
122 quality of  $R^2 = 0.999998$  and  $0.99998$  with root mean square errors of 1.15 and 3.98 ppm.  
123 Calibrations and data processing were carried out according to Fietzek et al. (2014) with the  
124 exception that, here, the interpolation between the pre- and the post-deployment calibration  
125 polynomial was carried out according to the sensor's absolute run-time between the two  
126 calibrations.

127 During the field deployment, the sensor was powered from the nearby pier. Data were stored  
128 internally on its data logger. The sensor was configured to carry out a 2 min zeroing every 6 h. A  
129 flushing interval duration of 55 min was used to analyze the data during recovery from zero to  
130 ambient values. During the subsequent measurement interval, a 10 s mean of the 1 Hz raw data  
131 was stored every minute.

132 The HydroC<sup>®</sup> was equipped with a flow-head allowing for passive diffusion of seawater to the  
133 sensor's membrane through a circumferential orifice along the cylindrical sensor housing. In order  
134 to improve the data quality under the given configuration and deployment conditions,  
135 determination and correction of the sensor's response time (RT) were given special attention (see  
136 Appendix A for further information). The sensor's in situ RT was determined to be  $546 \pm 208$  s  
137 (mean  $\pm$  SD) and the final *p*CO<sub>2</sub> series was response time corrected assuming a constant RT of  
138 546 s.

139 We conclude a general uncertainty for the final *p*CO<sub>2</sub> series in this study of 2.5% of reading as the  
140 standard deviation of the *p*CO<sub>2</sub> measurements. This value is comprised of the accuracy of drift  
141 corrected HydroC<sup>®</sup> *p*CO<sub>2</sub> data of approximately 1% of reading as found within Fietzek et al. (2014)  
142 and the uncertainty estimate of 1.5% of reading related to the actual RT influences (see Appendix  
143 A).

### 144 **2.3 Discrete sampling**



145 Over the course of the deployment, a total of 31 seawater samples for DIC and TA were taken at  
146 the sensor suite through snorkeling. Sampling was conducted twice a week in the hours following  
147 sunrise and solar noon. On a third day, duplicate sampling was conducted in the hour following  
148 solar noon. Corresponding sampling results were averaged to improve the quality of the  
149 measurements. Salinity of the water samples was measured in a laboratory at GEOMAR using a  
150 conductometer (SG 7/8, Mettler Toledo, Switzerland). Subsequently, the samples were poisoned  
151 with mercury chloride following the recommendations by Dickson et al. (2007). DIC (precision  $\pm$   
152  $3 \mu\text{mol kg}^{-1}$ ) was measured by coulometry using a SOMMA instrument (University of Rhode  
153 Island, USA) and TA (precision  $\pm 6 \mu\text{mol kg}^{-1}$ ) was determined with a VINDTA titrator (Marianda  
154 GmbH, Germany) following Dickson et al. (2007).

155 In parallel to all DIC and TA samplings, another set of seawater samples was taken and frozen for  
156 measurement of phosphate and silicate concentrations. Total phosphate (precision  $0.1 \mu\text{mol kg}^{-1}$ )  
157 and total silicate (precision  $0.2 \mu\text{mol kg}^{-1}$ ) concentrations were measured using a QuAAtro auto-  
158 analyzer with an XY-2 sampler (SEAL Analytical GmbH, Germany).

#### 159 **2.4.1 Correction for Organic Alkalinity**

160 The  $p\text{CO}_2$  in the discrete sample was calculated from measured DIC, TA, total phosphate and total  
161 silicate using the first and second carbonate system dissociation constants for brackish waters from  
162 Millero (2006) and the dissociations constants of HF and  $\text{HSO}_4^-$  of Perez and Fraga (1987) and  
163 Dickson (1990), respectively, with the R package Seacarb (Lavigne and Gattuso, 2013).

164 A critical point for the calculation of carbonate chemistry in waters containing significant amounts  
165 of dissolved organic matter, in the following referred to as DOC, is the contribution of organic  
166 acid-base components to the TA (Cai et al., 1998; Kuliński et al., 2014 and Yang et al., 2015). This  
167 organic TA contribution ( $\text{TA}_{\text{org}}$ ) is not reflected in models employed to interpret titration data nor  
168 in equations routinely used to perform carbonate system calculations. The classical concept, i.e.  
169 two out of four measureable carbonate system parameters are sufficient to calculate the remaining,  
170 is limited if TA is one of the measured parameters and the sample contains high amounts of DOC.  
171 In such cases, the TA value determined by titration can significantly exceed the amount of TA  
172 contributed by the inorganic acid-base components. This hinders an accurate quantification of the  
173 inorganic alkalinity and thereby affects the calculation of other carbonate system parameters.



174 Kuliński et al. (2014) demonstrated that the  $p\text{CO}_2$  calculated from TA and DIC is typically 100 -  
175 200  $\mu\text{atm}$  lower than the measured  $p\text{CO}_2$  in open waters of the Baltic Sea. This deviation is not  
176 observed if  $p\text{CO}_2$  is calculated from measured DIC and pH data (Fig. 2), which are unaffected by  
177 the  $\text{TA}_{\text{org}}$  contribution. Two aspects of the present study therefore require the consideration of  
178  $\text{TA}_{\text{org}}$ : (i)  $\text{TA}_{\text{org}}$  explains the observed differences between  $p\text{CO}_2$  measured in situ and  $p\text{CO}_2$   
179 calculated from DIC, TA, silicate and phosphate of discrete samples (Fig. 2) and (ii)  $\text{TA}_{\text{org}}$  needs  
180 to be considered when other carbonate system parameters ( $\text{pH}_T$ , DIC,  $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}}$ ) are calculated  
181 from the TA and  $p\text{CO}_2$  time series.

182 The offset between measured and calculated  $p\text{CO}_2$  caused by  $\text{TA}_{\text{org}}$  increases towards higher  $p\text{CO}_2$   
183 levels. This could be repeatedly observed during another measuring campaign in Kiel Bay  
184 (Hiebenthal et al., 2017, Fig. 2). To furthermore unravel the difference in observed versus  
185 calculated  $p\text{CO}_2$  for typical Kiel Bay conditions ( $S = 16$ ,  $T = 18\text{ }^\circ\text{C}$ ,  $\text{DOC} = 300\text{ }\mu\text{mol kg}^{-1}$ ,  $\text{TA} =$   
186  $1950\text{ }\mu\text{mol kg}^{-1}$ ), we qualitatively reproduced the impact of  $\text{TA}_{\text{org}}$  on the carbonate system by a  
187 modelling approach using regional  $\text{TA}_{\text{org}}$  properties reported by Kuliński et al. (2014). Our  
188 modelling approach revealed an offset between measured and observed  $p\text{CO}_2$  that increases with  
189  $\text{CO}_2$  partial pressure and reaches up to 300  $\mu\text{atm}$  at  $p\text{CO}_2$  levels around 2000  $\mu\text{atm}$  (Fig. 2, solid  
190 line). A more detailed description of the modelling approach is given in Appendix B.

191 For the calculation of carbonate system parameters ( $\text{pH}$ , DIC,  $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}}$ ) from TA and  $p\text{CO}_2$   
192 data, we consequently corrected the TA time series originally based on titration measurements for  
193 a  $\text{TA}_{\text{org}}$  contribution. Therefore we used 18 discrete seawater samples taken at 1 m depth right next  
194 to a constantly deployed HydroC<sup>®</sup>  $\text{CO}_2$  sensor at GEOMAR pier in the inner Kiel Bay, 2 km south  
195 of the above described experimental site between March and December 2015 (Hiebenthal et al.,  
196 2017). The water samples were poisoned with  $\text{HgCl}_2$  (Dickson et al., 2007) within 15 min and  
197 stored until measurement of DIC,  $\text{pH}_T$  and TA at the Leibniz Institute for Baltic Sea Research,  
198 Warnemünde, Germany. DIC was analyzed with a SOMMA system at  $15\text{ }^\circ\text{C}$ . TA was determined  
199 by an open-cell titration at  $20\text{ }^\circ\text{C}$ . Certified reference materials provided by Andrew Dickson's  
200 laboratory were measured in parallel for quality assurance. The  $\text{pH}_T$  of each water sample was  
201 determined spectrophotometrically at  $25\text{ }^\circ\text{C}$  with unpurified m-cresol purple as indicator dye  
202 (Hammer et al., 2014). Phosphate and silicate concentrations used for the 2015 samples were





203 measure after Grasshoff 1999 and sampled approximately 240 m from GEOMAR pier (Hiebenthal  
204 et al., 2017).

205 The  $TA_{org}$  fraction measured in Kiel inner Bay, determined as the difference between TA measured  
206 and TA calculated from DIC and  $pH_T$ , at GEOMAR pier 2015 was  $0.84 \pm 0.0005\%$  (mean  $\pm$  SE),  
207 corresponding to a contribution between approximately 8 and  $30 \mu\text{mol kg}^{-1}$ . We chose to consider  
208 this conservative range for the carbonate chemistry calculations instead of the values determined  
209 during the 2013 deployment,  $0.48 \pm 0.28\%$  (mean  $\pm$  SE). The reason for using the 2015 value is  
210 that it was determined from measurements of TA, DIC and  $pH_T$  in the same water samples  
211 (Hiebenthal et al., 2017), thereby avoiding the additional uncertainty and noise in the data due to  
212 a spatio-temporal mismatch between  $pCO_2$  sensor and discrete sample data of the 2013 field  
213 deployment.

## 214 **2.5 Seawater carbonate chemistry**

215 We used a model approach based on discrete water sample- and salinity data to estimate total  
216 alkalinity (TA) from salinity (S). Given the obvious changes particularly in phosphate and salinity  
217 around September 1<sup>st</sup> (Fig. 3A-B), two separate TA-S regressions were calculated for August and  
218 September (Fig. 4, Tab. 1). The slopes and intercepts were used to derive total alkalinity from the  
219 salinity time series. Both regressions were highly significant with p-values  $< 0.001$ ,  $R^2 = 0.64$  and  
220  $0.92$  for August and September respectively and standard deviations of the residuals  $< 15 \mu\text{mol}$   
221  $\text{kg}^{-1}$  (Fig. 4). The two intercepts for August and September are notably different by  $100 \mu\text{mol kg}^{-1}$   
222 while the two slopes are similar ( $\sim 40 \mu\text{mol kg}^{-1}$ ). An organic-free TA range was calculated  
223 ( $TA_{inorg}$ ) by subtracting constant organic alkalinity contributions of 8 and  $30 \mu\text{mol kg}^{-1}$  (lower and  
224 upper  $TA_{org}$  limits in 2015 measurements at GEOMAR pier; see 2.4) from the TA time series.

## 225 **2.6 Calculation of the regional atmospheric $pCO_2$**

226 Half-hourly measured  $CO_2$  mole fractions in dry air from the German Federal Environment  
227 Agency (Umweltbundesamt), Station Westerland,  $8.3082^\circ\text{E}$  and  $54.9250^\circ\text{N}$ , were averaged for  
228 the months August (08<sup>th</sup> – 31<sup>st</sup> 2013) and September (01<sup>st</sup> – 27<sup>th</sup> 2013):  $391 \pm 7$  and  $395 \pm 14$  ppm  
229 (mean  $\pm$  SD). Thereof  $pCO_2$  in wet air (100% relative humidity at SST) of 385 and  $388 \mu\text{atm}$  for  
230 August and September, respectively, were derived at local measurement conditions; i.e. using an  
231 averaged sea surface temperature ( $18.4 \pm 0.6$  and  $16.1 \pm 1.0^\circ\text{C}$ ) and ambient pressure readings





232 (1019.6 ± 4.2 and 1015.7 ± 7.5 mbar; both parameters from GEOMAR meteorological station,  
233 Fig. 1A) as well as the salinity measured in this study (15.6 ± 0.7 and 15.9 ± 1.0).

## 234 **2.7 Inferential statistics**

235 Daily means, maxima, minima as well as day-night peak-to-peak amplitudes and daily duration of  
236 undersaturation for calcite and aragonite (in hours) (mean ± SD) for the months of August and  
237 September were compared using Mann-Whitney U tests. Statistical analyses were conducted with  
238 Statistica 7 (Statsoft, USA).

## 239 **3 Results**

### 240 **3.1 Salinity, water temperature, total silicate and total phosphate observations**

241 Salinity did not show circadian patterns and the daily mean salinity was not significantly different  
242 between August and September (Mann-Whitney U,  $p > 0.05$ , see Appendix C for detailed  
243 statistics), with  $15.65 \pm 0.7$  and  $15.89 \pm 1.01$  (mean ± SD), respectively (Fig. 3A). The total  
244 alkalinity (TA), derived from salinity, varied between 1934 and 1956  $\mu\text{mol kg}^{-1}$  during the 2  
245 months, with a SD of 41  $\mu\text{mol kg}^{-1}$ . As a marker of seasonality, temperature daily means, minima,  
246 maxima were all significantly lower in September compared to August (Mann-Whitney U,  $p <$   
247  $0.001$ , see Appendix C), with drops of 2.3 °C, 2.2 °C and 3 °C, respectively (Tab. 2, Fig. 3A, 4A).  
248 The daily variation amplitude was significantly reduced in September by 0.3 °C compared to  
249 August (Mann-Whitney U,  $p < 0.01$ , see Appendix C). Total silicate was not significantly different  
250 between August and September:  $19.0 \pm 4.9 \mu\text{mol kg}^{-1}$  and  $18.8 \pm 5.4 \mu\text{mol kg}^{-1}$  (Mann-Whitney  
251 U,  $p > 0.05$ , see Appendix C). Total phosphate was significantly different between August and  
252 September:  $0.7 \pm 0.14 \mu\text{mol kg}^{-1}$  and  $5.9 \pm 3.7 \mu\text{mol kg}^{-1}$  (Mann-Whitney U,  $p < 0.001$ , see  
253 Appendix C).

### 254 **3.2 $p\text{CO}_2$ and $[\text{O}_2]$ observations**

255 The daily mean (± SD)  $p\text{CO}_2$  of  $628 \pm 114 \mu\text{atm}$  in August and  $652 \pm 193 \mu\text{atm}$  in September (Tab.  
256 2) remained always above the regional atmospheric  $p\text{CO}_2$  of approximately 387  $\mu\text{atm}$ . The mean  
257 daily minimum and maximum  $p\text{CO}_2$  values were  $334 \pm 119 \mu\text{atm}$  and  $1151 \pm 328 \mu\text{atm}$  in August  
258 and  $373 \pm 139 \mu\text{atm}$  and  $1097 \pm 336 \mu\text{atm}$  (mean ± SD) in September, respectively (see Tab. 2,



259 Figs. 3C, 5B). A modest and non-significant increase of the daily means was observed between  
260 August and September (+ 22  $\mu\text{atm}$ ) as well as a non-significant average decrease of the day-night  
261 variability by 93  $\mu\text{atm}$  (Mann-Whitney U,  $p > 0.05$ , see Appendix C) (Tab. 2). A high  $p\text{CO}_2$  event  
262 was observed between September 8<sup>th</sup> and September 12<sup>th</sup> with a peak of the daily mean  $p\text{CO}_2$  to  
263 1166  $\mu\text{atm}$  on September 9<sup>th</sup>. On this day, a maximum  $p\text{CO}_2$  of 1839  $\mu\text{atm}$  was observed at  
264 04:30 a.m. (see Fig. 3C).

265 The daily mean  $[\text{O}_2]$  most of the time remained below the seawater saturation threshold (~260 to  
266 290  $\mu\text{mol kg}^{-1}$ ) (Fig. 3D, Tab. 2). However, supersaturation due to photosynthesis was regularly  
267 observed between noon and sunset in August. Significant decreases of the daily average, maximum  
268 and minimum  $[\text{O}_2]$  by 47  $\mu\text{mol kg}^{-1}$ , 64  $\mu\text{mol kg}^{-1}$ , 35  $\mu\text{mol kg}^{-1}$ , respectively, were observed in  
269 September (Mann-Whitney U, all  $p < 0.001$ , see Appendix C for details) (Tab. 2, Fig. 5C), with  
270 an abrupt  $[\text{O}_2]$  decrease occurring on Sept. 8<sup>th</sup>, in parallel to a sudden decrease in temperature by  
271 approximately 2 °C (Fig. 3A-D). A significant decrease of the day-night amplitude by 29  $\mu\text{mol kg}^{-1}$   
272 was observed from August to September (Mann-Whitney U,  $p = 0.008$ , Appendix C). The  
273 threshold for hypoxia (60  $\mu\text{mol kg}^{-1}$ ) is never undercut (see Fig. 3D); the minimum daily mean  
274 concentration observed during the two months was 140  $\mu\text{mol kg}^{-1}$ .

### 275 3.3 Derived carbonate chemistry parameters

276 Times series for  $\text{pH}_T$ , DIC,  $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}}$  (Fig. 6) were derived from modeled  $\text{TA}_{\text{inorg}}$  (Fig. 4) and  
277 measured  $p\text{CO}_2$  and analyzed for daily means, minima, maxima and diel peak-to-peak amplitudes  
278 (mean  $\pm$  SD) with  $\text{TA}_{\text{org}} = 8 \mu\text{mol kg}^{-1}$  and  $\text{TA}_{\text{org}} = 30 \mu\text{mol kg}^{-1}$  (Tab. 1). Since the differences in  
279 the calculated parameters between the  $\text{TA}_{\text{org}} = 8 \mu\text{mol kg}^{-1}$  and the  $\text{TA}_{\text{org}} = 30 \mu\text{mol kg}^{-1}$  estimates  
280 are too small to be recognizable in Fig. 6, only results for the mean  $\text{TA}_{\text{org}} = 19 \mu\text{mol kg}^{-1}$  are  
281 shown. Overall, we observe a slight and non-significant (Mann-Whitney U,  $p > 0.05$ , see Appendix  
282 C for details) decrease in daily means of DIC and  $\text{pH}_T$  between August and September by 11  $\mu\text{mol}$   
283  $\text{kg}^{-1}$  and 0.02  $\text{pH}_T$  units respectively (Tab. 1). In parallel, we observe a non-significant decrease of  
284 the amplitudes of the diel variations in DIC of 21  $\mu\text{mol kg}^{-1}$  (Mann-Whitney U,  $p > 0.05$ , see  
285 Appendix C) and  $\text{pH}_T$  of approximately 0.05  $\text{pH}_T$  units (Mann-Whitney U,  $p > 0.05$ , see Appendix  
286 C) and (Tab. 1, Fig. 5). All these observations are coherent with the changes in  $p\text{CO}_2$  previously  
287 described.



288 Daily means of  $\Omega_{\text{arag}}$  are close to the saturation threshold: between 1.3 and 1.4 in August and 1.2  
289 in September (Tab. 1). For both,  $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}}$ , we observe a significant decrease in daily mean  
290 values (Mann-Whitney U, all  $p < 0.01$ , see Appendix C) and a marginally significant decrease of  
291 diel amplitudes between August and September (Mann-Whitney U, all  $p < 0.1$ , see Appendix C)  
292 (Tab. 1, Fig. 5). In both isoforms, the amplitudes decrease results from a significant reduction of  
293 the daily maxima (Mann-Whitney U,  $p = 0.001$ , see Appendix C) with the minima remaining  
294 constant (Mann-Whitney U,  $p > 0.05$ , see Appendix C) (Tab. 1, Fig. 5). On average, the seawater  
295 was undersaturated with respect to aragonite for approximately 6 hours per days in August and  
296 approximately 9 hours per day in September (Tab. 1). Similarly, seawater was undersaturated with  
297 respect to calcite for approximately 30 min and approximately 1 hour 30 min in August and  
298 September, respectively (Tab. 1). Only one full day of undersaturation with respect to aragonite  
299 was observed on September 9<sup>th</sup> during the high  $p\text{CO}_2$  event (Fig. 5).

300 Over the whole measurement period, the consideration of organic alkalinity contributions has little  
301 effect on the derived  $\text{CO}_2$  system parameters (mean value differences:  $20 \mu\text{mol kg}^{-1}$  DIC,  $< 2 \mu\text{mol}$   
302  $\text{kg}^{-1}$   $[\text{CO}_3^{2-}]$  and negligible effect on omegas and  $\text{pH}_T$ ). The only noticeable difference when taking  
303  $\text{TA}_{\text{org}}$  into account was an increase of time of undersaturation for  $\Omega_{\text{arag}}$  and  $\Omega_{\text{calc}}$  in September of  
304 approximately 25 min and approximately 10 min, respectively.

## 305 4 Discussion

### 306 4.1 $p\text{CO}_2$ , carbonate chemistry and $\text{O}_2$

307 Monthly averages of  $p\text{CO}_2$  close to the seafloor as presented in this study ( $\sim 640 \mu\text{atm}$ ; Tab. 1)  
308 were more than 50% above atmospheric  $p\text{CO}_2$ . In 2011, Saderne et al. (2013), used similar  
309 technologies as in our study in a seaweed dominated bed of Eckernförde Bay (adjacent to Kiel  
310 Bay, Western Baltic) and found significantly lower weekly mean  $p\text{CO}_2$  values ( $\sim 390 \mu\text{atm}$  in July,  
311  $\sim 240 \mu\text{atm}$  in August and  $420 \mu\text{atm}$  in September, excluding an upwelling event, Saderne et al.,  
312 2013). Accordingly, the day-night amplitudes of  $p\text{CO}_2$  observed in the present study ( $764 \pm 310$   
313  $\mu\text{atm}$ , overall mean  $\pm$  SD) are 3 to 4 times higher than observed during “normal” days by Saderne  
314 et al. (2013) ( $243 \pm 95 \mu\text{atm}$ ) in the neighboring Eckernförde Bay in 2011. This reflects a  
315 characteristic of the marine carbonate system: Equal DIC variations will induce stronger  $p\text{CO}_2$   
316 variations at high “baseline”  $p\text{CO}_2$  levels compared to lower  $p\text{CO}_2$  levels. The source of this pattern



317 is the reduced buffering capacity of the carbonate system at a high  $p\text{CO}_2$  “baseline”. Accordingly,  
318 Saderne et al. (2013) found extreme  $p\text{CO}_2$  variations of approximately 1700  $\mu\text{atm}$  during an  
319 upwelling event that lifted the “baseline”  $p\text{CO}_2$  to approximately 1600  $\mu\text{atm}$ , although the DIC  
320 variations due to plant photosynthesis remained rather unchanged by the upwelling. Likewise, the  
321 amplitude of the diel DIC variations during our study (145  $\mu\text{mol kg}^{-1}$  in August and 124  $\mu\text{mol kg}^{-1}$   
322 in September, see Tab.1 and Fig. 5) were of the same magnitude as what had been observed in  
323 Eckernförde Bay before and after upwelling (141  $\mu\text{mol kg}^{-1}$  and 106  $\mu\text{mol kg}^{-1}$ ,  
324 respectively, Saderne et al., 2013).

325 Average  $\text{O}_2$  concentrations were below saturation in August and September 2013, with a  
326 significant decrease occurring in September (monthly means of 89.4%  $[\text{O}_2]_{\text{sat}}$  and 68.8%  $[\text{O}_2]_{\text{sat}}$   
327 for August and September respectively). However, we note that at no point of our survey the  
328 threshold of hypoxia (~22% saturation; 60  $\mu\text{mol kg}^{-1}$ ) was reached. The significant  $\text{O}_2$  decrease in  
329 September co-occurred with an increase in phosphate and a change in DIC to TA regression. This  
330 can possibly be explained by a rapid degradation of the seagrass shoots observed in September and  
331 a possible shift of the habitat from an auto- to a heterotrophic system.

#### 332 4.2 Implications for mussel calcification in a seagrass meadow

333 We found pronounced variations of  $\Omega_{\text{calc}}$  and  $\Omega_{\text{arag}}$  on a daily basis, e.g., resulting in 5.7 to 8.8 h  
334 of undersaturation for aragonite per day in the water body right above the mussel patch.

335 As expected, daytime photosynthesis counters water corrosiveness caused by heterotrophic  
336 processes, while at night water corrosiveness is reinforced by respiration. Waldbusser et al. (2014)  
337 demonstrated that saturation states (and therefore  $[\text{CO}_3^{2-}]$ ) are the parameters affecting the larval  
338 development and growth of *Mytilus galloprovincialis* and *Crassostrea gigas*. On young *M. edulis*  
339 Hiebenthal et al. (2013) found a negative correlation between growth and  $\Omega$  or  $[\text{CO}_3^{2-}]$ . Thomsen  
340 et al. (2015) confirmed these findings in larvae and juveniles. With a meta-analysis including all  
341 past work on mussel populations from Kiel Bay, they found that the critical  $\text{CO}_3^{2-}$  concentration  
342 below which calcification starts to decline was 80  $\mu\text{mol kg}^{-1}$  (although they specified that the  
343 directly related ratio  $[\text{H}^+]/[\text{HCO}_3^-]$  is likely to be the controlling parameter for calcification,  
344 Thomsen et al. 2015). In our survey, mussels were exposed to  $[\text{CO}_3^{2-}]$  below this threshold for 12  
345  $\pm 5.2$  h per day in August and  $15.3 \pm 5.4$  h per day in September (mean  $\pm$  SD). Comparing these



346 findings to the shorter durations of aragonite (5-9 h per day) and calcite (~1 h per day)  
347 undersaturation implies that reduced calcification rates might already occur during periods with  
348 low, yet oversaturated calcium carbonate concentrations. However, the consequences of these  
349 successions of intense corrosive stress and stress relaxation on the juvenile and adults forming the  
350 mussel patch is still under debate. On mussel larvae, Frieder et al., 2013 showed that the negative  
351 effects of elevated  $p\text{CO}_2$  (~1500  $\mu\text{atm}$ ) on *Mytilus galloprovincialis* disappear, if diel variations  
352 of 500  $\mu\text{atm}$  were added, although this effect was not observed for *Mytilus californianus*. Wahl et  
353 al. (2017) found that in laboratory and mesocosm experiments calcification of blue mussels is  
354 significantly higher during daytime, when photosynthetic activity of macrophytes creates  
355 favorable calcification conditions. However, in field studies they did not detect a positive net effect  
356 of the co-occurrence with macrophytes on the calcification of mussels (Wahl et al. 2017).  
357 Furthermore, Thomsen et al. (2013) showed that high food availability, particularly in Kiel Bay,  
358 can circumvent the effects of acidification in mussels.

359

## 360 **Conclusion**

361 Our study demonstrates how essential it is to place more effort in measuring the carbonate  
362 chemistry variations in nearshores habitats, and highlights the need to include variability when  
363 investigating the impact of OA on benthic organisms. We emphasize that continuous carbonate  
364 system observations in benthic habitats are possible but challenging due to the high spatio-  
365 temporal variability and organic alkalinity contributions. However, with the here applied  
366 combination of in situ sensor measurements, laboratory analyses of discrete water samples, and  
367 modelling elements we were able to distinguish daily oscillations and shifts of averages (across  
368 weeks) of several seawater chemistry parameters. This approach specifically allowed for a  
369 temporal quantification of dissolution threshold undercuts *M. edulis* experiences in this exemplary  
370 site of Kiel Bay.

## 371 **Appendix A: HydroC<sup>®</sup> response time and related signal processing**

372 The entire HydroC<sup>®</sup>  $p\text{CO}_2$  time series has a total of 187 zeroings and related flush intervals. A first  
373 order kinetics model was fitted to every of the HydroC<sup>®</sup>'s signal recoveries from its zero value to  
374 ambient partial pressure over an 55 min flush interval to obtain sensor response times (see Fiedler



375 et al. 2013). The fit interval was set to extend over 55 min to be around 6 times as large as the  
376 sensor's response time to allow for reasonable fitting of the exponential increase. In general the  
377 carbonate system at the site was characterized by a strongly varying baseline featuring very steep  
378  $p\text{CO}_2$  gradients over the course of the day with slopes of up to  $-54 \mu\text{atm}/\text{min}$ . Therefore the  $p\text{CO}_2$   
379 signal recovery from zero to ambient during the 187 flush intervals was often superimposed with  
380 a changing background partial pressure. These adverse conditions hamper the response time  
381 determination by means of a first order kinetics fit. We therefore flagged and not considered further  
382 the recoveries providing the worst fit results, which indicates a bad match between model and real  
383 signal: (i) the fits characterized by the largest 10% of root mean square (RMS) residuals of the  
384 fitted curve and the real signal as well as (ii) the fits with the largest 10% of the uncertainty of the  
385 fitted response time.

386 Finally a total of 157 fit results were considered providing an average response time ( $t_{63}$ ) of  
387  $546 \pm 208 \text{ s}$  with an RMS of the fit function of  $6.0 \pm 3.1 \mu\text{atm}$  and a fit uncertainty for the response  
388 time of  $1.2 \pm 0.4 \text{ s}$ . The average response time found is in good agreement with a  $t_{63}$  of  
389  $553 \pm 8 \mu\text{atm}$  as determined during a dedicated laboratory test with a similar sensor setup at  $14.5^\circ\text{C}$   
390 water temperature. The large standard deviation of the averaged in situ response times (i.e. 208 s)  
391 is likely caused (i) by the influence of the strongly varying background  $p\text{CO}_2$  on the data to be  
392 fitted and (ii) by the variability of the water exchange in front of the membrane within the flow-  
393 head as caused by i.e. changes in the ambient water currents. Against the large variability in the  
394 determined response times, a temperature dependence of the  $t_{63}$  can be neglected as well as a  
395 potential response deceleration caused by fouling on the membrane, which was only observed to  
396 a very small extend after the deployment.

397 The response time (RT) correction according to Miloshevich et al. (2004) and Fiedler et al. (2013)  
398 was carried out with a constant response time of 546 s to obtain the final  $p\text{CO}_2$  series. The  $p\text{CO}_2$   
399 data were additionally RT-corrected with a reduced ( $\text{RT}_{\text{short}} = 546 - 208 = 338 \text{ s}$ ) and an extended  
400 response time ( $\text{RT}_{\text{long}} = 546 + 208 = 754 \text{ s}$ ). In order to estimate the uncertainty of the final  $p\text{CO}_2$   
401 time series, the differences between the  $\text{RT}_{\text{long}}$ - and the RT-corrected as well as between the RT-  
402 and the  $\text{RT}_{\text{short}}$ -corrected  $p\text{CO}_2$  time series were determined. They both provide a small average  
403  $\Delta p\text{CO}_2$  of  $0.8 \mu\text{atm}$  (0.06% of reading) and a corresponding standard deviation of  $10 \mu\text{atm}$  (1.5%  
404 of reading). The standard deviation is influenced by short periods characterized by large  $p\text{CO}_2$   
405 gradients where the RT-correction has the largest effect; i.e. at  $130 \mu\text{atm}/\text{min}$  over 3 minutes



406 (54  $\mu\text{atm}/\text{min}$  in the original, non-RT-corrected data) the steepest  $p\text{CO}_2$  decline of the series was  
407 observed in the early morning of August 22<sup>nd</sup> at around 4:40 causing the maximum observed  
408 individual  $\Delta p\text{CO}_2$  of  $-172 \mu\text{atm}$  or 23% of reading.

409 The standard deviation of the  $\Delta p\text{CO}_2$  (1.5% of reading) is used as a measure for the  $p\text{CO}_2$   
410 uncertainty in this study related to the response time influences. Not considering the response time  
411 and applying a related correction, would have forced us to continue the analysis with a less  
412 realistic, “smoothed” data set that showed temporally delayed as well as amplitude-damped  $p\text{CO}_2$   
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## 420 **Appendix B**

421 We implemented a model to estimate the potential error associated to  $\text{CO}_2$  system calculations, in  
422 case one of the input parameters is titrated TA including organic acid-base components.

423 Hence, we firstly calculated the carbonate system at varying DIC and constant TA, salinity, and  
424 temperature. In this case the derived carbonate system parameters (i.e.  $p\text{CO}_2$ ) reflect values as  
425 calculated from TA and DIC measured in discrete samples.

426 Organic contribution to TA ( $\text{TA}_{\text{org}}$ ) is estimated based on the relation reported by Kuliński et al.  
427 (2014) for the Baltic Sea, which approximates  $\text{TA}_{\text{org}}$  from the proton concentration  $[\text{H}^+]$ , the  
428 amount of DOC, a bulk dissociation constant ( $K_{\text{DOM}}$ ) and the fraction of DOC ( $f$ ) acting as a carrier  
429 of weakly acidic groups

$$430 \quad \text{TA}_{\text{org}} = \frac{K_{\text{DOM}} \cdot f \cdot \text{DOC}}{[\text{H}^+] + K_{\text{DOM}}}$$

431 This  $\text{TA}_{\text{org}}$  estimate is a side-specific approximation since  $K_{\text{DOM}}$  and  $f$  ( $2.94 \times 10^{-8} \text{ mol kg}^{-1}$  and  
432 0.14, respectively) are characteristic for the actual DOM composition. Further,  $K_{\text{DOM}}$  is currently  
433 only reported for  $T=25^\circ\text{C}$  and no salinity-dependence was investigated. Therefore, this model is  
434 only a qualitative approximation of the carbonate system in high DOC waters.





435 The inorganic TA fraction can be approximated as  $TA_{inorg} = TA - TA_{org}$ . This  $TA_{inorg}$  together with  
 436 DIC can be used to calculate the “correct”  $pCO_2$  ( $pCO_{2,sensor}$ ) as it would also be obtained from  
 437 direct observations, since  $TA_{inorg}$  represents the share of the alkalinity which is covered by the  
 438 dissociation constants and equilibrium reactions implemented in the routinely applied carbonate  
 439 system models (i.e.  $CO_{2sys}$ , seacarb).

440 Finally, the  $TA_{org}$  estimate needs to be refined. Above, it was estimated from the proton  
 441 concentration, which itself was derived from TA and DIC. Now,  $TA_{inorg}$  is the better input  
 442 parameter to calculate this proton concentration. Thus, we recalculate first  $TA_{org}$  to get a refined  
 443 value ( $TA_{org,ref}$ ). The other carbonate system parameters, including  $pCO_{2,sensor,ref}$ , are calculated  
 444 with  $TA_{org,ref}$ . This refinement procedure was repeated iteratively, until no significant changes  
 445 occurred between the iterative steps. The finally obtained  $pCO_{2,sensor,ref}$  would reflect direct  $pCO_2$   
 446 measurements performed with a dedicated in situ sensor.

447 Model output:

448 The model predicts an increase in the deviation between  $pCO_2$  measured in situ ( $pCO_{2,sensor,ref}$ ) and  
 449  $pCO_2$  values obtained by calculations from discrete sample TA and DIC towards  $pCO_2$  levels  
 450 around 2000  $\mu atm$  as depicted in Fig. 2 (input parameters:  $S = 16$ ,  $T = 18$  °C,  $DOC = 300$   $\mu mol$   
 451  $kg^{-1}$ ,  $TA = 1950$   $\mu mol$   $kg^{-1}$ ,  $K_{DOM}$  and  $f$  from Kuliński et al. (2014),  $CO_2$  system constants from  
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459

## 460 Appendix C: Mann-Whitney U tests details

461 Result table for the Mann Whitney tests comparing August and September data listed in Table 2.

	U	Z	p-value	August n	September n
Mean Temperature	2	5.71	<0.01	20	26
Min. Temperature	5	5.64	<0.01	20	26
Max. Temperature	1	5.73	<0.01	20	26
$\Delta$ Temperature	133	2.80	0.01	20	26



Mean Salinity	198	-1.36	0.17	20	26
Min. Salinity	196	-1.41	0.16	20	26
Max. Salinity	186	-1.63	0.10	20	26
$\Delta$ Salinity	252	-0.17	0.87	20	26
Total Silicate	114	0.100	0.920	13	18
Total Phosphate	0	-4.665	<0.001	13	18
Mean $p\text{CO}_2$	255	0.10	0.92	20	26
Min. $p\text{CO}_2$	220	-0.88	0.38	20	26
Max. $p\text{CO}_2$	233	0.59	0.56	20	26
$\Delta p\text{CO}_2$	220	0.88	0.38	20	26
Mean $[\text{O}_2]$	67	4.758	<0.001	24	26
Min. $[\text{O}_2]$	121	3.709	<0.001	24	26
Max. $[\text{O}_2]$	68	4.738	<0.001	24	26
$\Delta[\text{O}_2]$	176	2.641	0.008	24	26
$\text{TA}_{\text{org}} = 8$					
	U	Z	p-value	August n	September n
Mean $\text{pH}_T$	241	0.41	0.68	20	26
Min. $\text{pH}_T$	246	-0.30	0.76	20	26
Max. $\text{pH}_T$	212	1.05	0.29	20	26
$\Delta\text{pH}_T$	215	0.99	0.32	20	26
Mean DIC	254	0.12	0.90	20	26
Min. DIC	227	-0.72	0.47	20	26
Max. DIC	203	1.25	0.21	20	26
$\Delta$ DIC	198	1.36	0.17	20	26
Mean $[\text{CO}_3^{2-}]$	172	1.94	0.05	20	26
Min. $[\text{CO}_3^{2-}]$	225	0.76	0.44	20	26
Max. $[\text{CO}_3^{2-}]$	153	2.36	0.02	20	26
$\Delta[\text{CO}_3^{2-}]$	181	1.74	0.08	20	26
Mean $\Omega_{\text{arag}}$	157	2.27	0.02	20	26
Min. $\Omega_{\text{arag}}$	213	1.03	0.30	20	26
Max. $\Omega_{\text{arag}}$	150	2.43	0.02	20	26
$\Delta \Omega_{\text{arag}}$	176	1.85	0.06	20	26
time $\Omega_{\text{arag}} < 1$	176	-1.85	0.06	20	26
Mean $\Omega_{\text{calc}}$	167	2.05	0.04	20	26
Min. $\Omega_{\text{calc}}$	215	0.99	0.32	20	26
Max. $\Omega_{\text{calc}}$	152	2.38	0.02	20	26



$\Delta \Omega_{\text{calc}}$	178	1.81	0.07	20	26
time $\Omega_{\text{calc}} < 1$	212	-1.05	0.29	20	26
TA <sub>org</sub> = 30					
	U	Z	p-value	August n	September n
Mean pH <sub>T</sub>	241	0.41	0.68	20	26
Min. pH <sub>T</sub>	246	-0.30	0.76	20	26
Max. pH <sub>T</sub>	212	1.05	0.29	20	26
$\Delta \text{pH}_T$	215	0.99	0.32	20	26
Mean DIC	253	0.14	0.89	20	26
Min. DIC	228	-0.70	0.49	20	26
Max. DIC	203	1.25	0.21	20	26
$\Delta \text{DIC}$	197	1.38	0.17	20	26
Mean [CO <sub>3</sub> <sup>2-</sup> ]	172	1.94	0.05	20	26
Min. [CO <sub>3</sub> <sup>2-</sup> ]	225	0.76	0.44	20	26
Max. [CO <sub>3</sub> <sup>2-</sup> ]	151	2.40	0.02	20	26
$\Delta [\text{CO}_3^{2-}]$	181	1.74	0.08	20	26
Mean $\Omega_{\text{arag}}$	157	2.27	0.02	20	26
Min. $\Omega_{\text{arag}}$	213	1.03	0.30	20	26
Max. $\Omega_{\text{arag}}$	149	2.45	0.01	20	26
$\Delta \Omega_{\text{arag}}$	176	1.85	0.06	20	26
time $\Omega_{\text{arag}} < 1$	175	-1.87	0.06	20	26
Mean $\Omega_{\text{calc}}$	168	2.03	0.04	20	26
Min. $\Omega_{\text{calc}}$	214	1.01	0.31	20	26
Max. $\Omega_{\text{calc}}$	152	2.38	0.02	20	26
$\Delta \Omega_{\text{calc}}$	178	1.81	0.07	20	26
time $\Omega_{\text{calc}} < 1$	218	-0.9	0.4	20	26

462

## 463 Acknowledgements

464 The authors would like to thank particularly Dr. Todd Martz and his team from the Scripps  
 465 Institution of Oceanography (San Diego, USA) for providing the salinity / [O<sub>2</sub>] / T° sensor package  
 466 and for their precious technical assistance. We also wish to thank the Kiel Marine Organism  
 467 Culture Centre (KIMOCC) of the Kiel Cluster of excellence “Future Ocean”; Sebastian Fessler  
 468 from GEOMAR for the TA / DIC sample measurements; Dr. Bernd Schneider and Stefan Bucker



469 from the IOW are thanked for valuable discussions with respect to carbonate system analysis in  
470 the Baltic Sea as well as for the inter comparison between TA / DIC / pH measurements; Prof.  
471 Peter Herman from the NIOZ Royal Netherlands Institute for Sea Research for providing access  
472 to the nutrient analyzer; Dr. Jörn Thomsen for his comments on the manuscript; the research divers  
473 from GEOMAR among which are Prof. Martin Wahl, Dr. Christian Pansch, Dr. Yvonne Sawall  
474 and Christian Lieberum; the personnel of the “Seebar am Seebad Düsternbrook” restaurant for  
475 providing electricity to the sensors as well as the Kiel early morning nudist club for its cooperation  
476 in providing access to the Seebar. This work has been funded by the Kiel Cluster of excellence  
477 “Future Ocean”.

478



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597 Fig. 1. A. Map of the inner Kiel Bay with study site and the GEOMAR station. B. Photo of the  
598 sensor suite at the measurement site.

599 Fig. 2. Deviation between observed and calculated  $p\text{CO}_2$  ( $\Delta p\text{CO}_2$ ) as a function of observed  $p\text{CO}_2$   
600 illustrating the influence of  $\text{TA}_{\text{org}}$  on carbonate system determinations. Dashed lines represent  
601 linear regressions of the respective data. **Black triangles:**  $\Delta p\text{CO}_2 = p\text{CO}_2 \text{ sensor} - p\text{CO}_2$  (TA, DIC)  
602 for the benthic seagrass deployment of this study,  $n = 30$ . The  $\Delta p\text{CO}_2$  can be explained by a  
603 combination of the influence of an organic TA contribution of  $0.49 \pm 1.47\%$  with measurement  
604 uncertainties and sampling errors (spatio-temporal mismatches). **Dark grey diamonds:**  $\Delta p\text{CO}_2 =$   
605  $p\text{CO}_2 \text{ sensor} - p\text{CO}_2$  (TA, DIC) based on corrected HydroC<sup>®</sup> measurements and discrete samples  
606 taken at GEOMAR pier in 2015 (Hiebenthal et al., 2017). DIC, TA and  $\text{pH}_T$  were measured in the  
607 same water samples. The  $\Delta p\text{CO}_2$  is due to a  $\text{TA}_{\text{org}}$  fraction of  $0.84 \pm 0.0005\%$  (mean  $\pm$  SD). **Grey**  
608 **circles:**  $\Delta p\text{CO}_2 = p\text{CO}_2 \text{ sensor} - p\text{CO}_2$  (DIC,  $\text{pH}_T$ ), based on corrected sensor data and discrete  
609 samples taken at GEOMAR pier during the same period in 2015,  $n = 18$  (Hiebenthal et al., 2017).  
610 There is no  $p\text{CO}_2$  dependency of the  $\Delta p\text{CO}_2$ , because neither DIC nor  $\text{pH}_T$  are impacted by  $\text{TA}_{\text{org}}$ ,  
611  $R^2 = 0.005$ . **Solid black line:** Difference between observed and calculated  $p\text{CO}_2$  from a model  
612 including  $\text{TA}_{\text{org}}$  contributions typical for Baltic Sea water (for details see Appendix B).

613 Fig. 3. Time series for observed parameters: A: Salinity (black) and temperature (grey), 10 min  
614 sampling interval B: Total phosphate (green) and silicate (red) concentration from 31 discrete  
615 sampling events at the sensor location. C:  $p\text{CO}_2$  at 1-min measurement interval (solid line) and  
616 24h moving average (dashed line). D: Dissolved oxygen concentration at 10-min measurement  
617 interval (solid green line) and as 24h moving average (dashed green line). Also shown is the  
618 oxygen saturation concentration calculated from the water temperature and salinity (black). The  
619 straight solid red line represents the hypoxia threshold of  $60 \mu\text{mol kg}^{-1}$ .

620 Fig. 4. Alkalinity (TA) time series (black line) modeled from salinity using the regression  
621 equations from August and September. Grey lines represent the  $\text{TA}_{\text{inorg}}$  time series after subtraction  
622 of the organic alkalinity contribution of 8 and  $30 \mu\text{mol kg}^{-1}$  from TA, respectively. Triangles  
623 (August) and dots (September) represent TA of 31 discrete samples used for the regressions. The  
624 sample from the 1st of September at 6:40 (open dot) was not considered for the regression. Insert  
625 panel: Linear regressions of TA as function of salinity in discrete samples for the months of August



626 in blue (n = 14) and September in red (n= 16), see Table 1 for equations and statistics. Dashed  
627 lines are 90% confidence intervals.

628 Fig. 5. Hourly means ( $\circ$ )  $\pm$  standard deviation (-) for the months of August (grey) and September  
629 (black) for Temperature (A.),  $p\text{CO}_2$  (B.) and  $[\text{O}_2]$  (C.). Hourly mean ranges and maximum upper  
630 as well as minimum lower standard deviations (-) calculated using  $\text{TA}_{\text{org}}$  contributions of 8 and 30  
631  $\mu\text{mol kg}^{-1}$  for  $\text{pH}_T$  (D.), DIC (E.),  $[\text{CO}_3^{2-}]$  (F.),  $\Omega_{\text{arag}}$  (G.) and  $\Omega_{\text{calc}}$  (H.). The dissolution thresholds  
632 of the  $\Omega$  values are depicted as solid red lines in panel G. and H.

633 Fig. 6. Derived time series of carbonate system parameters:  $\text{pH}_T$  (A), Dissolved inorganic carbon  
634 (DIC, B.) and saturation states for aragonite ( $\Omega_{\text{arag}}$ , light brown) and calcite ( $\Omega_{\text{calc}}$ , dark brown)  
635 with dissolution threshold  $\Omega = 1$  (red line, C.). All time series are calculated from  $p\text{CO}_2$  (10 min  
636 interval) and total alkalinity with a mean organic contribution of  $19 \mu\text{mol kg}^{-1}$ .

637 Fig. 7. Carbonate ion concentration,  $[\text{CO}_3^{2-}]$ , calculated from  $p\text{CO}_2$  (10 min interval) and total  
638 alkalinity with a mean organic contribution of  $19 \mu\text{mol kg}^{-1}$ . The red line represents a side specific  
639  $[\text{CO}_3^{2-}]$  threshold of  $80 \mu\text{mol kg}^{-1}$  below which calcification declines in mussels according to  
640 Thomsen et al., 2015.

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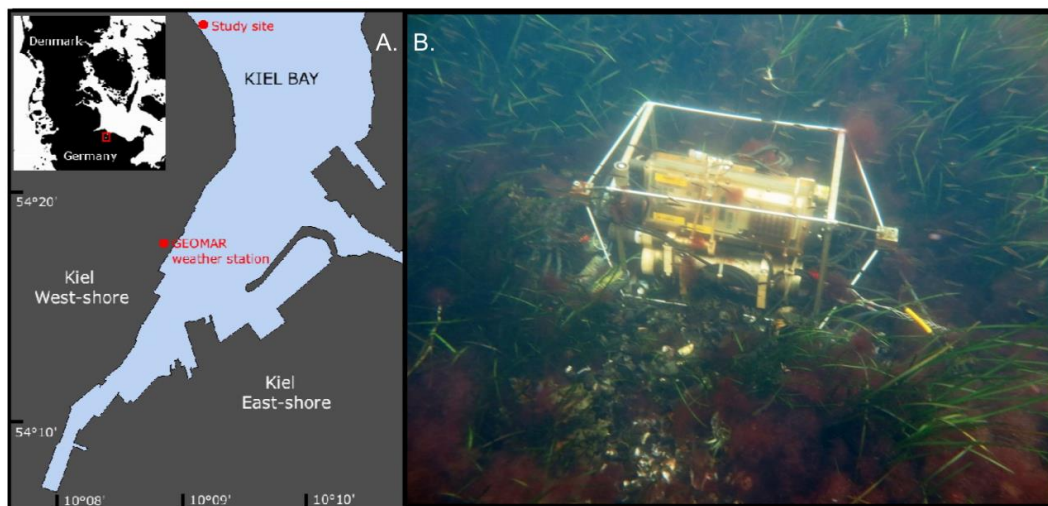
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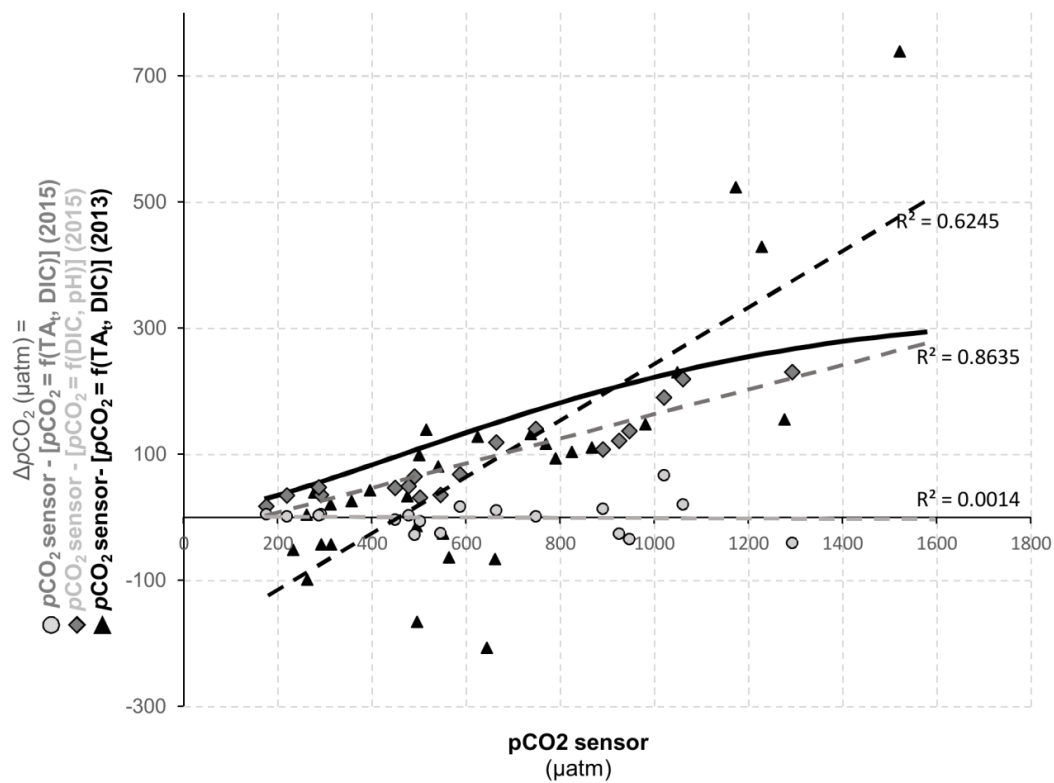
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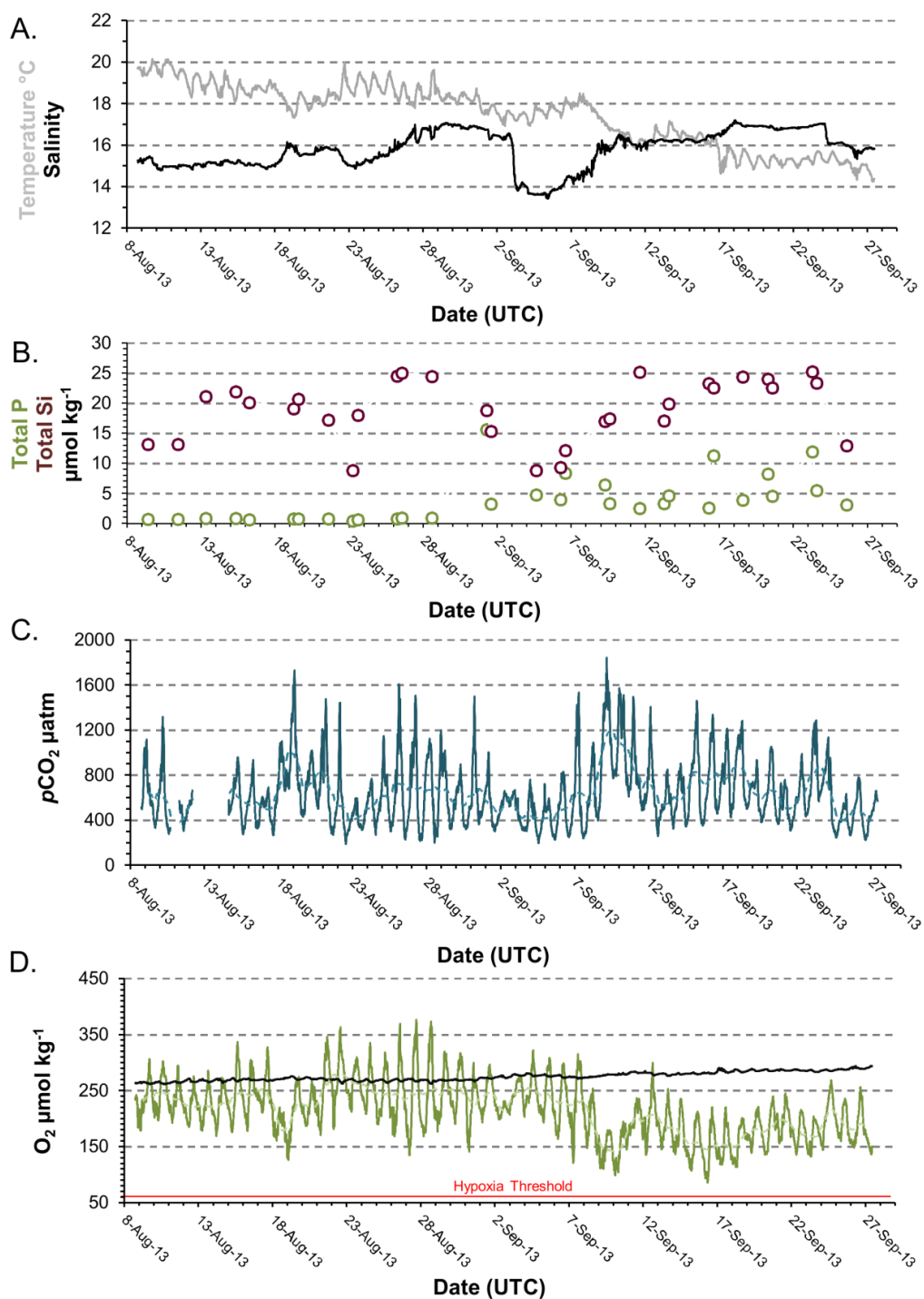
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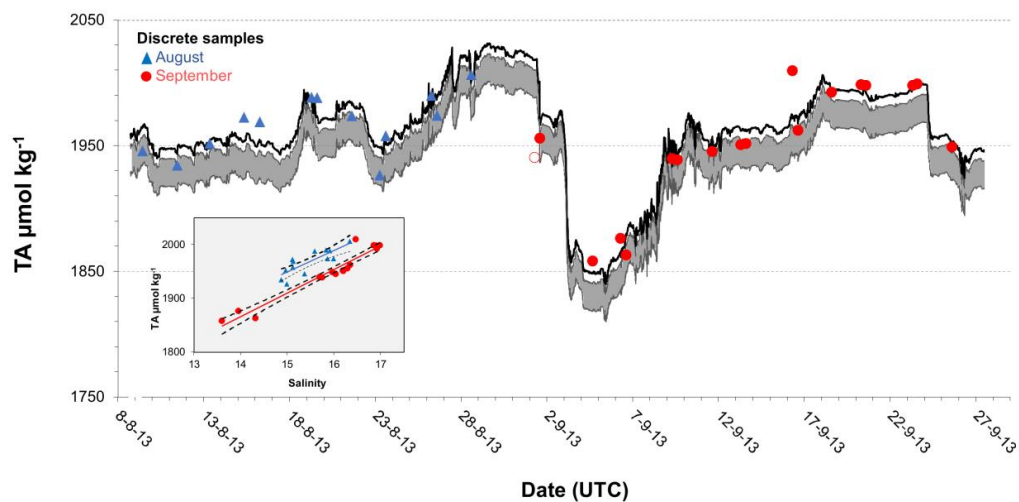
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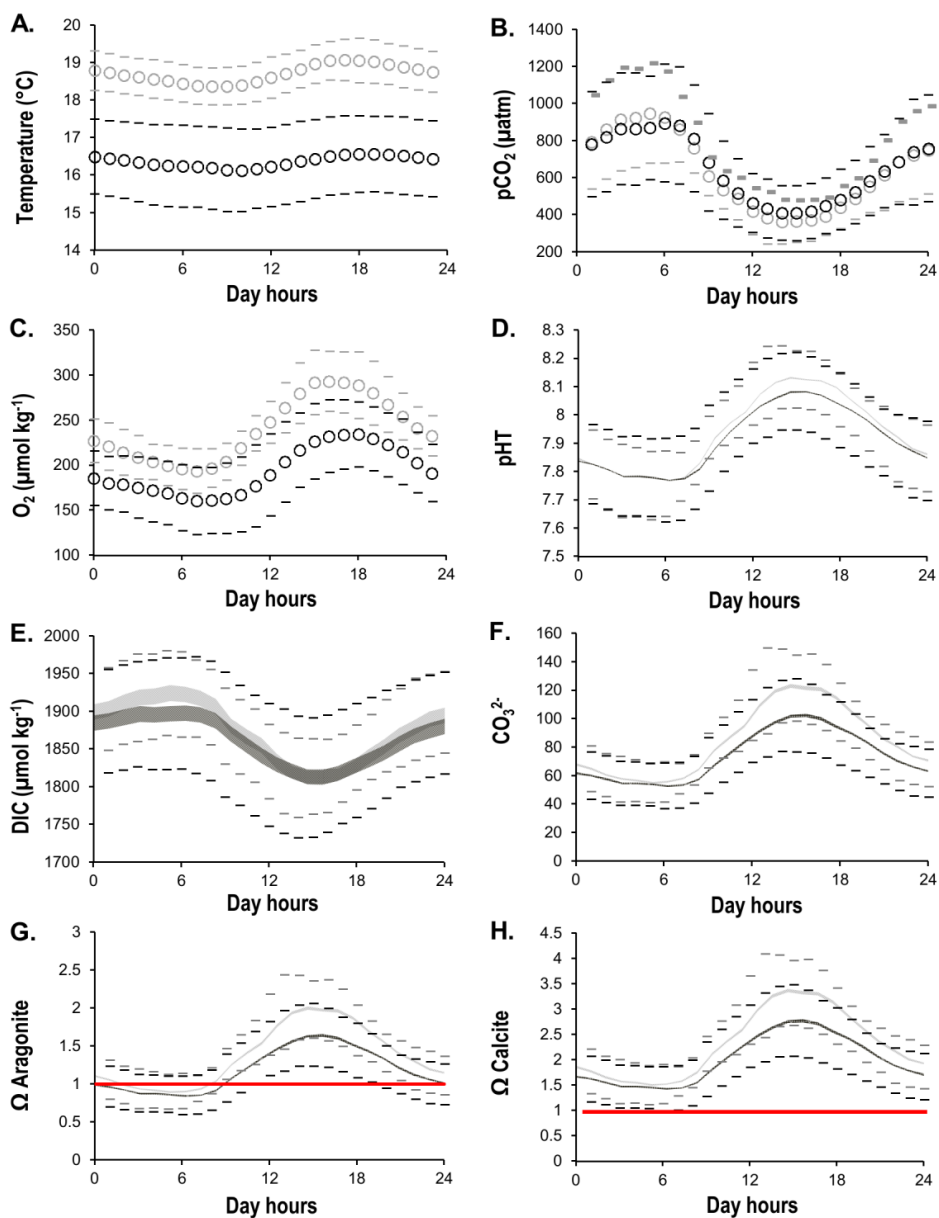
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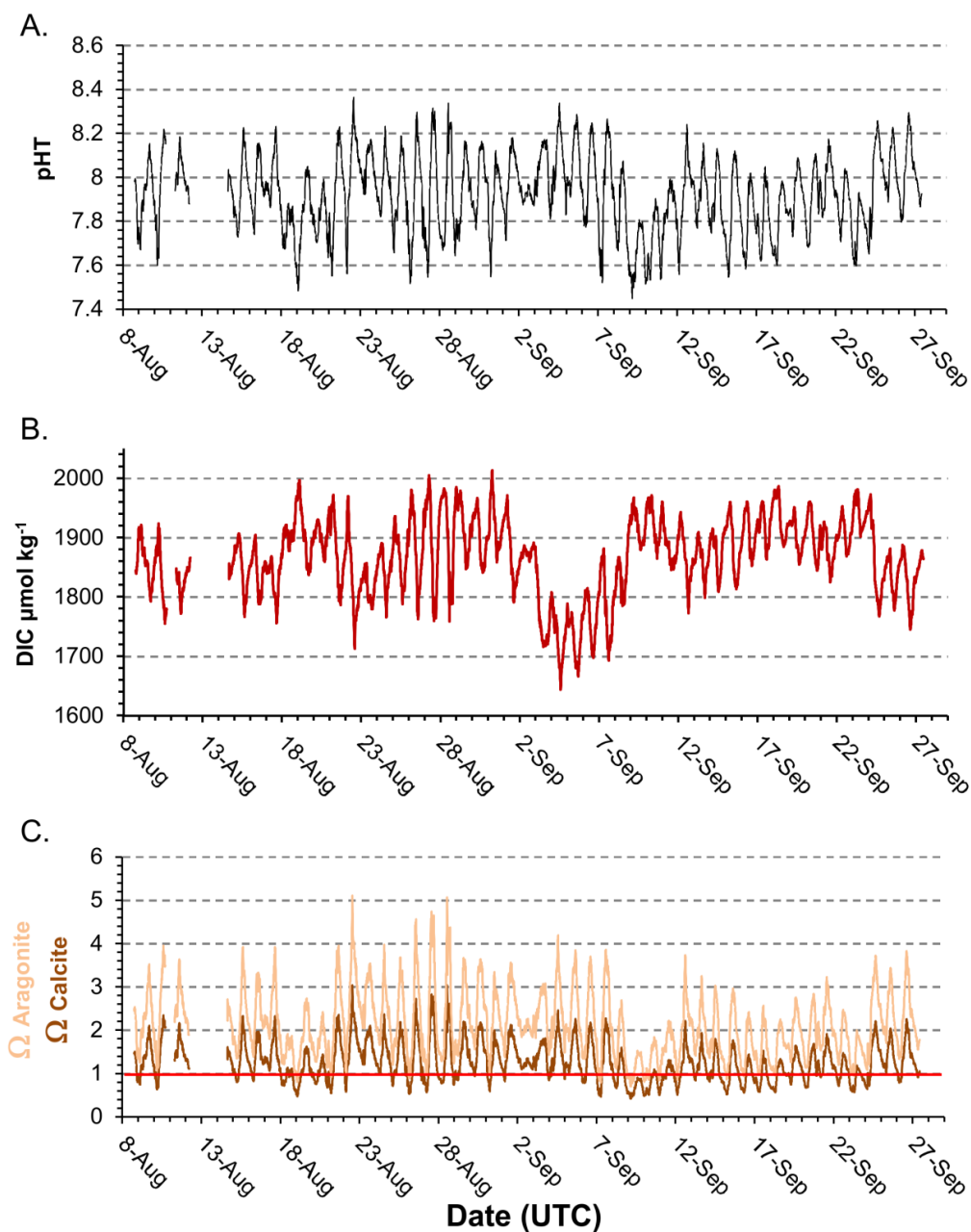
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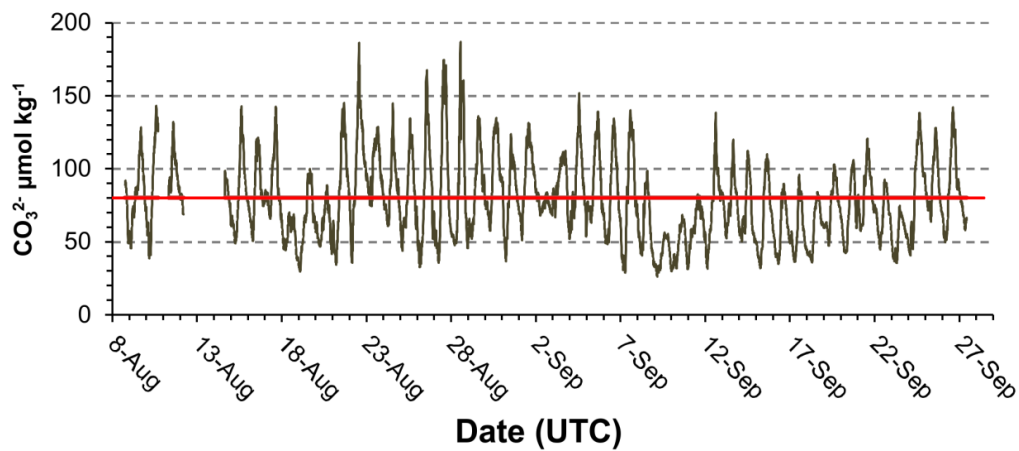
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