

39 **CO₂ Sensor description and data processing:**

40 Data were measured with a HydroC® CO₂ generation II sensor with the serial number CO2-1011-002
41 manufactured by Kongsberg Maritime Contros GmbH and purchased by GEOMAR in 2012. A SBE 5T
42 underwater pump (Sea-Bird electronics, Bellevue, Washington, USA) was used to continuously
43 provide water to the sensor's membrane at a flow rate of nominally around 100 ml/s. Design and
44 validation of the sensor are described in Fietzek et al. (2014).

45 During the time interval February 2015 until April 2016 the sensor was calibrated by the
46 manufacturer as described in Fietzek et al. (2014). See table 1 for a summary of calibration conditions
47 and results as used for data processing.

48

49 *Table 1: Calibration identifier, dates, water temperatures, ranges as well as number of pCO₂ levels*
50 *and values regarding the quality of the calibration polynomial fit (root mean square error, RMSE, and*
51 *R²) as used within data processing. Calibrations labelled 'a'/'b' are the pre- / post – deployment*
52 *calibrations. Data were processed block-wise for each of these two deployment time intervals. A 1.b*
53 *calibration was not possible, since the sensor experienced an electrical damage originating from an*
54 *underwater plug during the deployment.*

55 **temperature irregularities were observed during the 2.a calibration. Since there was a minor zero*
56 *drift of only -0.36 µatm observed between 2.a and 2.b (~238 days between 2.a and 2.b, ~138 days of*
57 *absolute sensor runtime between 2.a and 2.b), it was decided to only use the polynomial of 2.b during*
58 *processing.*

Id.	Date	Water temperature (T, °C)	Calibration range (pCO ₂ , µatm)	# pCO ₂ levels during calibration	RMSE (µatm)	R ²
1.a	13.02.2015	11.5	200 – 1,000	4	0,27	0.9999995
2.a	25.08.2015	13*	200 – 3,000	6	3.16	0.9999931
2.b	19.04.2016	13	200 – 3,000	6	2.63	0.9999952

59

60 Raw data were present in the form of multiple data files downloaded from the internal logger of the
61 sensor. Sensor settings with respect to interval (i.e. zero, flush and measure) and logging durations
62 were the same during the two deployments (for the vast majority of the time). Zero gas
63 measurements lasting 2 minutes were carried out every 12 hours and measurement data was saved
64 every minute as a 10 sec mean value of 1 Hz data (for the vast majority of the time). The clock of the
65 sensor's internal data logger was set to UTC. The following processing steps were conducted:

66 **1. Data preparation:**

- 67 a. Warm-up phases included in the data (not yet stabilized control temperature) were
68 removed.
- 69 b. Data from times of a clocked or turned-off underwater pump were removed through
70 filtering for low pump power values (e.g. during 20.-26.10.2015 the pump intake was
71 clocked by dead shrimp).
- 72 c. During 21.-25.09.2015 the HydroC® sensor was used elsewhere and no data is
73 considered for this period.

74

75 **2. Data processing:**

- 76 a. Data processing and sensor drift correction were carried out as described in Fietzek
77 et al. (2014) using the pre- and post-deployment-calibration for the deployment 1
78 and 2 respectively (tab. 1) as well as the information from the zeroing
79 measurements.
- 80 b. NDIR detectors overestimate CO₂ readings in the presence of water vapor due to
81 pressure broadening effects. In addition to the processing described in Fietzek et al.
82 2014, we therefore used an equivalent pressure within the calculations. It was
83 determined using an empirically found band-broadening coefficient (Welles and
84 McDermitt 2005) of $\hat{\alpha}_v=1.48$ and 1.62 for deployments 1 and 2 respectively.
- 85 c. In case of data gaps between two zeroing events that were more than 24 hours
86 apart, the course of the preceding or following two zero signals was linearly
87 extrapolated forward or backward respectively. (In Fietzek et al. 2014 only linear
88 interpolation between zero signals was applied as the deployment was shorter and
89 did not show large interruptions.)
- 90 d. Successful processing demands for clear zero signals. Therefore the first 30 seconds
91 from every zeroing interval (due to the fact that it contains the signal drop from
92 ambient measurement to zero) were discarded in order to obtain smooth zero
93 measurements.
- 94 e. In order to purge the data set from signal recovery periods (i.e. flush interval), 10 min
95 were filtered after every preceding zeroing.
96 Six additional signal recoveries were manually removed during deployment
97 interval 2. These recoveries likely originate from the fact that the water pump of the
98 sensor was started manually a while after the sensor was placed back in the water
99 after cleaning. Under these conditions sensor data flagged as “measurement data”
100 shows an unwanted signal recovery as well.

101 **3. Data finishing:**

- 102 a. Data between 03.10.2015 ~1:00 and 09.10.2015 ~1:00 were removed due to an
103 unusual drift pattern observed between the reference and the raw signal with a
104 questionable effect on the data quality during this period.

105 In Fietzek et al. 2014 a deviation between HydroC® sensors and reference system data
106 of $-0.6 \pm 3.0 \mu\text{atm}$ with an RMSE of $3.7 \mu\text{atm}$ was found resembling an estimated measurement
107 uncertainty (RMSE) of approx. 1% from reading. Despite the additional processing steps described
108 above, we conservatively assume the uncertainty of the $p\text{CO}_2$ data discussed here to be greater 1%
109 of reading due to the fact that we only used one calibration within each deployment and since the
110 measuring range observed during this deployment is larger than the one encountered in Fietzek et al.
111 2014.

112

113

114 **TA, DIC and pH determination:**

115 For laboratory seawater analysis of carbonate chemistry on each sampling day two 250 ml Niskin
116 bottles were filled from one 3 L volume of seawater sampled at 1 m depth in ~0.5 m distance of the
117 HydroC® deployment site using a water sampler that opens at the desired depth. The samples were

118 poisoned with 100 µl HgCl₂ (after Dickson et al., 2007) each within 15 min and stored until the
119 measurement of DIC, pH and TA at the Leibniz Institute for Baltic Sea Research (IOW), Warnemünde,
120 Germany. Seawater samples were transported to the IOW in four batches and measured thereafter:
121

122 Batch1: sampling between 25.02. and 20.04.2015 (6 samples), measured on 15.06.2015

123 Batch2: sampling between 29.04. and 11.08.2015 (11 samples), measured on 30.09./05.10.2015

124 Batch3: sampling between 21.08. and 20.11.2015 (10 samples), measured on 04.12./09.12.2015

125 Batch4: sampling between 03.12. and 21.12.2015 (2 samples), measured on 21.09./22.9.2016

126

127 One of the 250 ml volume bottles of seawater from each sampling was used for the measurement of
128 DIC and the other one for TA titration and pH measurement. DIC was analyzed with a SOMMA
129 system (MARIANDA, Kiel, Germany) at 15 °C using a CO₂ Coulometer Model 5014 (UIC Inc., P.O. Box
130 863, Joliet, IL 60434, U.S.A.). TA was determined by an open-cell titration at 20 °C according to
131 Dickson et al. (2007). Certified reference materials provided by Andrew Dickson's laboratory (Scripps
132 Institution of Oceanography, UC San Diego, USA) were used for calibration. The pH of each water
133 sample was determined spectrophotometrically at 25 °C with unpurified m-cresol purple as indicator
134 dye (Mosley et al. 2004) with the instrument described in Carter et al. 2013. The uncertainties
135 related to these laboratory based analyses of DIC, TA and pH are ±2 µmol/kg, ±5 µmol/kg and ±0.01
136 respectively as validated by measurements of certified reference material.

137

138

139 **Nutrient data:**

140 Water samples for nutrient analysis (silicate and phosphate) were taken during a 2015 sampling time
141 series from "F.B. Polarfuchs" with a water sampler at 0 m water depth in the inner Kiel fjord at
142 position N 54°19.69', E 10°09.060' (station "Wittlingskuhle"), which is approx. 240 m from the
143 HydroC® deployment site. From each seawater sampling volume one 60 ml water subsample was
144 frozen on the day of sampling and measured after Grasshoff (1999), later.

145

146 The nutrient data were interpolated linearly in time and from that the molar concentrations of
147 silicate and phosphate derived at the time of the discrete sampling of the CO₂ system parameters.
148 Obviously, this approximation contains an uncertainty due to a local mismatch between the sampling
149 location of the discrete TA/DIC/pH samples and the nutrient samples (in depth and position).
150 Furthermore, sampling was assumed to have happened at noon every day. Despite these
151 shortcomings, using this nutrient information is still better than none and the effect of nutrients
152 within the following analysis of pCO₂ derived from DIC and pH is small (<1 µatm).

153

154

155

156

157 **Carbonate chemistry calculations and final discussion:**

158 The program CO2SYS (originally by Lewis and Wallace, 1998) and the equilibration constants of
159 Millero 2006 were used to determine the $p\text{CO}_2$ from the input parameters DIC and TA, DIC and pH as
160 well as TA and pH.

161 The clear deviation between the $p\text{CO}_2(\text{DIC, TA})$ and $p\text{CO}_2(\text{DIC, pH})$ is caused by the influence of
162 organic compounds unwantedly affecting the determination of the alkalinity of the sample (c.f. TA_{org} ,
163 Kulinski et al. 2014). Furthermore, using nutrients in the calculations has a clear effect on $p\text{CO}_2(\text{DIC, TA})$. The best option to validate the continuous $p\text{CO}_2$ data of the sensor is a comparison with the
164 $p\text{CO}_2(\text{DIC, pH})$. Maximum error investigations on the samples using CO2SYS and assuming
165 uncertainties of $\pm 2 \mu\text{mol/kg}$ for DIC and ± 0.01 for pH lead to a mean relative uncertainty of
166 $\pm 2.6\%$ ($\pm 0.05\%$ standard deviation) for the $p\text{CO}_2$ derived from DIC and pH.
167

168 We observe an offset \pm standard deviation between the $p\text{CO}_2$ of the HydroC[®] sensor ($p\text{CO}_{2,\text{Sensor}}$) and
169 the $p\text{CO}_2(\text{DIC, pH})$ of $(-22.3 \pm 12.1) \mu\text{atm}$ (equivalent to $-7.2\% \pm 3.2\%$ of reading) during deployment 1
170 ($n=8$) and $(-78.4 \pm 32.3) \mu\text{atm}$ (equivalent to $-11.2\% \pm 5.6\%$ of reading) during deployment 2 ($n=10$,
171 one outlier likely caused by the pH measurement was not considered). For the comparison we used
172 the sensor value temporally closest to the sampling time of the discrete sample and averaged it with
173 the value(s) ± 1 min to it.

174 The final $p\text{CO}_2$ data set we are reporting ($p\text{CO}_{2,\text{Sensor}+\text{offset}}$) is the processed $p\text{CO}_2$ of the sensor from
175 deployment 1 $+22.3 \mu\text{atm}$ and the processed $p\text{CO}_2$ from deployment 2 $+78.4 \mu\text{atm}$, since the offsets
176 found between $p\text{CO}_{2,\text{Sensor}}$ and $p\text{CO}_2(\text{DIC, pH})$ are larger than the maximum uncertainty determined
177 for $p\text{CO}_2(\text{DIC, pH})$. The fact that the $p\text{CO}_2$ difference between the $p\text{CO}_{2,\text{Sensor}+\text{offset}}$ and the $p\text{CO}_2(\text{DIC, pH})$ plotted over $p\text{CO}_{2,\text{Sensor}+\text{offset}}$ does not show a significant slope (=‘There is no clear $p\text{CO}_2$ -
178 dependency in the observed offset’), further supports us in the assumption that this step is a feasible
179 mean to obtain an improved and validated $p\text{CO}_2$ time series. After this additional correction the
180 resulting mean difference \pm standard deviation between the $p\text{CO}_{2,\text{Sensor}+\text{offset}}$ and the $p\text{CO}_2(\text{DIC, pH})$ is
181 $(0 \pm 12.1) \mu\text{atm}$ for deployment 1 and $(0 \pm 32.3) \mu\text{atm}$ for deployment 2 respectively. In relative
182 terms, the standard deviation corresponds to 2.7 % of sensor reading for deployment 1 and 3.4 % of
183 sensor reading for deployment 2 respectively. Therefore we conclude these values of **2.7 % and**
184 **3.4 % of reading as the uncertainties of the final $p\text{CO}_2$ data sets** ($p\text{CO}_{2,\text{Sensor}+\text{offset}}$) related to the
185 discrete $p\text{CO}_2(\text{DIC, pH})$ determinations (uncertainty $\pm 2.6\%$) for deployment 1 and 2 respectively.
186

187

188 References:

189 Carter, B. R., Radich, J. A., Doyle, H. L. and Dickson, A. G. (2013): An automated system for
190 spectrophotometric seawater pH measurements. *Limnol. Oceanogr.: Methods* 11, 16–27.

191 Dickson, A. G., Sabine, C. L. and Christian, J. R. (2007): Guide to Best Practices for Ocean CO_2
192 Measurements, PICES spec. publication 3.

193 Fietzek, P., B. Fiedler, T. Steinhoff, and A. Körtzinger (2014): In situ quality assessment of a novel
194 underwater $p\text{CO}_2$ sensor based on membrane equilibration and NDIR spectrometry. *J. Atmos.*
195 *Ocean. Technol.*, 31, 181–196.

- 196 Grasshoff, K., Kremling, K. and Ehrhardt, MG. (1999): Methods of Seawater Analysis (3rd Edition).
197 VCH Publishers. 632 pp.
- 198 Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H. and Pierrot, D. (2006): Dissociation
199 constants of carbonic acid in seawater as a function of salinity and temperature, *Mar. Chem.*,
200 100(1-2), 80–94, doi:10.1016/j.marchem.2005.12.001.
- 201 Mosley, L.M. , Husheer, S.L.G. and Hunter, K.A. (2004): Spectrophotometric pH measurement in
202 estuarines using thymol blue and m-cresol purple. *Mar. Chem.*, 91, 175–186
- 203 Kuliński, K., Schneider, B., Hammer, K., Machulik, U. and Schulz-Bull, D. (2014): The influence of
204 dissolved organic matter on the acid–base system of the Baltic Sea, *J. Mar. Syst.*, 132, 106–115,
205 doi:10.1016/j.jmarsys.2014.01.011, 2014.
- 206 Lewis, E. and Wallace, D. (1998) Program developed for CO₂ system calculations. ORNL/CDIAC-105.
207 Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of
208 Energy, Oak Ridge, Tennessee.
- 209 Welles, J. M., and D. K. McDermitt (2005): Measuring carbon dioxide in the atmosphere.
210 *Micrometeorology Agric. Syst.*, 287–320.
- 211