Kiel fjord carbonate chemistry data between 2015 (February) and 2016 (January)

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Sensor deployment, maintenance and discrete sampling:

A HydroC® CO_2 sensor was deployed from a pontoon at the waterfront of the GEOMAR west shore building into Kiel Fjord, Western Baltic Sea (Kiel, Germany; 54°19'48.78"N, 010° 8'59.44"E). Since the pontoon is floating the deployment depth of the sensor was constant at 1m. Data of two deployment intervals are published here:

1) February 2015 – May 2015
2) August 2015 – January 2016

In addition to the anti-fouling head installed in front of the membrane and the standard copper anti fouling cap installed on the stainless steel strainer pump intake, the sensor was equipped with a coarse plastic mesh to prevent clogging of the inflow by jellyfish and/or other large floating objects. Macrofoulers (mainly mussel and barnacle settlers) were removed and the sensor – including the sensor head – was cleaned weekly during summer season and biweekly during winter season. The sensor membrane was exchanged during routine maintenance at the manufacturer, Kongsberg Maritime Contros GmbH (Kiel, Germany, see calibration dates below).

Throughout 2015 a total of 29 discrete water samples for a laboratory based determination of total alkalinity (TA), dissolved inorganic carbon (DIC) and seawater pH were taken at the same location by means of Niskin bottles poisoned with $HgCl_2$ and analyzed (in agreement with the best practices procedures by Dickson et al. 2007) at Leibniz Institute for Baltic Sea Research (IOW), Warnemünde, Germany (details see below).

To enable a complete analysis of the carbonate chemistry during the times of the discrete samples nutrient data of silicate and phosphate were obtained from a 2015 sampling series where water samples were taken at the water surface in the inner Kiel fjord (details see below).

CO₂ Sensor description and data processing:

Data were measured with a HydroC® CO_2 generation II sensor with the serial number CO2-1011-002 manufactured by Kongsberg Maritime Contros GmbH and purchased by GEOMAR in 2012. A SBE 5T underwater pump (Sea-Bird electronics, Bellevue, Washington, USA) was used to continuously provide water to the sensor's membrane at a flow rate of nominally around 100 ml/s. Design and validation of the sensor are described in Fietzek et al. (2014).

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

Table 1: Calibration identifier, dates, water temperatures, ranges as well as number of pCO_2 levels and values regarding the quality of the calibration polynomial fit (root mean square error, RMSE, and R^2) as used within data processing. Calibrations labelled 'a'/'b' are the pre- / post – deployment calibrations. Data were processed block-wise for each of these two deployment time intervals. A 1.b calibration was not possible, since the sensor experienced an electrical damage originating from an underwater plug during the deployment.
[*]temperature irregularities were observed during the 2.a calibration. Since there was a minor zero drift of only -0.36 µatm observed between 2.a and 2.b (~238 days between 2.a and 2.b, ~138 days of absolute sensor runtime between 2.a and 2.b), it was decided to only use the polynomial of 2.b during 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

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

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

2. **Data processing:**
   a. Data processing and sensor drift correction were carried out as described in Fietzek et al. (2014) using the pre- and post-deployment-calibration for the deployment 1 and 2 respectively (tab. 1) as well as the information from the zeroing measurements.
   b. NDIR detectors overestimate CO_2 readings in the presence of water vapor due to pressure broadening effects. In addition to the processing described in Fietzek et al. 2014, we therefore used an equivalent pressure within the calculations. It was determined using an empirically found band-broadening coefficient (Welles and McDermitt 2005) of $â_v$=1.48 and 1.62 for deployments 1 and 2 respectively.
   c. In case of data gaps between two zeroing events that were more than 24 hours apart, the course of the preceding or following two zero signals was linearly extrapolated forward or backward respectively. (In Fietzek et al. 2014 only linear interpolation between zero signals was applied as the deployment was shorter and did not show large interruptions.)
   d. Successful processing demands for clear zero signals. Therefore the first 30 seconds from every zeroing interval (due to the fact that it contains the signal drop from ambient measurement to zero) were discarded in order to obtain smooth zero measurements.
   e. In order to purge the data set from signal recovery periods (i.e. flush interval), 10 min were filtered after every preceding zeroing.
   Six additional signal recoveries were manually removed during deployment interval 2. These recoveries likely originate from the fact that the water pump of the sensor was started manually a while after the sensor was placed back in the water after cleaning. Under these conditions sensor data flagged as "measurement data" shows an unwanted signal recovery as well.

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

In Fietzek et al. 2014 a deviation between HydroC® sensors and reference system data of -0.6 ± 3.0 µatm with an RMSE of 3.7 µatm was found resembling an estimated measurement uncertainty (RMSE) of approx. 1% from reading. Despite the additional processing steps described above, we conservatively assume the uncertainty of the pCO$_2$ data discussed here to be greater 1% of reading due to the fact that we only used one calibration within each deployment and since the measuring range observed during this deployment is larger than the one encountered in Fietzek et al. 2014**.**

TA, DIC and pH determination:

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

poisoned with 100 μl HgCl$_2$ (after Dickson et al., 2007) each within 15 min and stored until the measurement of DIC, pH and TA at the Leibniz Institute for Baltic Sea Research (IOW), Warnemünde, Germany. Seawater samples were transported to the IOW in four batches and measured thereafter:

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

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

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

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

One of the 250 ml volume bottles of seawater from each sampling was used for the measurement of DIC and the other one for TA titration and pH measurement. DIC was analyzed with a SOMMA system (MARIANDA, Kiel, Germany) at 15 °C using a CO$_2$ Coulometer Model 5014 (UIC Inc., P.O. Box 863, Joliet, IL 60434, U.S.A.). TA was determined by an open-cell titration at 20 °C according to Dickson et al. (2007). Certified reference materials provided by Andrew Dickson's laboratory (Scripps Institution of Oceanography, UC San Diego, USA) were used for calibration. The pH of each water sample was determined spectrophotometrically at 25 °C with unpurified m-cresol purple as indicator dye (Mosley et al. 2004) with the instrument described in Carter et al. 2013. The uncertainties related to these laboratory based analyses of DIC, TA and pH are ±2 μmol/kg, ±5 μmol/kg and ±0.01 respectively as validated by measurements of certified reference material.

Nutrient data:

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

The nutrient data were interpolated linearly in time and from that the molar concentrations of silicate and phosphate derived at the time of the discrete sampling of the CO$_2$ system parameters. Obviously, this approximation contains an uncertainty due to a local mismatch between the sampling location of the discrete TA/DIC/pH samples and the nutrient samples (in depth and position). Furthermore, sampling was assumed to have happened at noon every day. Despite these shortcomings, using this nutrient information is still better than none and the effect of nutrients within the following analysis of pCO$_2$ derived from DIC and pH is small (<1 μatm).

Carbonate chemistry calculations and final discussion:

The program CO2SYS (originally by Lewis and Wallace, 1998) and the equilibration constants of Millero 2006 were used to determine the pCO_2 from the input parameters DIC and TA, DIC and pH as well as TA and pH.

The clear deviation between the pCO_2(DIC, TA) and pCO_2(DIC, pH) is caused by the influence of organic compounds unwantedly affecting the determination of the alkalinity of the sample (c.f. TA_{org}, Kulinski et al. 2014). Furthermore, using nutrients in the calculations has a clear effect on pCO_2(DIC, TA). The best option to validate the continuous pCO_2 data of the sensor is a comparison with the pCO_2(DIC, pH). Maximum error investigations on the samples using CO2SYS and assuming uncertainties of ±2 µmol/kg for DIC and ±0.01 for pH lead to a mean relative uncertainty of ±2.6% (±0.05% standard deviation) for the pCO_2 derived from DIC and pH.

We observe an offset ± standard deviation between the pCO_2 of the HydroC® sensor ($pCO_{2,Sensor}$) and the pCO_2(DIC, pH) of (-22.3 ± 12.1) µatm (equivalent to -7.2% ± 3.2% of reading) during deployment 1 (n=8) and (-78.4 ± 32.3) µatm (equivalent to -11.2% ± 5.6% of reading) during deployment 2 (n=10, one outlier likely caused by the pH measurement was not considered). For the comparison we used the sensor value temporally closest to the sampling time of the discrete sample and averaged it with the value(s) ±1 min to it.

The final pCO_2 data set we are reporting ($pCO_{2,Sensor+offset}$) is the processed pCO_2 of the sensor from deployment 1 +22.3 µatm and the processed pCO_2 from deployment 2 +78.4 µatm, since the offsets found between $pCO_{2,Sensor}$ and pCO_2(DIC, pH) are larger than the maximum uncertainty determined for pCO_2(DIC, pH). The fact that the pCO_2 difference between the $pCO_{2,Sensor+offset}$ and the pCO_2(DIC, pH) plotted over $pCO_{2,Sensor+offset}$ does not show a significant slope (='There is no clear pCO_2-dependency in the observed offset'), further supports us in the assumption that this step is a feasible mean to obtain an improved and validated pCO_2 time series. After this additional correction the resulting mean difference ± standard deviation between the $pCO_{2,Sensor+offset}$ and the pCO_2(DIC, pH) is (0 ± 12.1) µatm for deployment 1 and (0 ± 32.3) µatm for deployment 2 respectively. In relative terms, the standard deviation corresponds to 2.7 % of sensor reading for deployment 1 and 3.4 % of sensor reading for deployment 2 respectively. Therefore we conclude these values of **2.7 % and 3.4 % of reading as the uncertainties of the final pCO_2 data sets** ($pCO_{2,Sensor+offset}$) related to the discrete pCO_2(DIC, pH) determinations (uncertainty ±2.6%) for deployment 1 and 2 respectively.

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