

Kiel fjord $p\text{CO}_2$ datasets between 2012 (July) and 2015 (January)

measured using a HydroC[®] $p\text{CO}_2$ sensor

C. Hiebenthal, P. Fietzek, J. Thomsen, V. Saderne, F. Melzner

Sensor deployment and maintenance:

The 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 three deployment intervals are published here:

- 1) July 2012 - December 2012
- 2) April 2013 - June 2013
- 3) November 2013 – January 2015

In addition to the standard copper anti fouling cap installed on the stainless steel strainer pump intake, the sensor was equipped with a coarse plastic mesh or a perforated plastic bottle 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 repeatedly cleaned. During deployment intervals 1 and 2 this procedure happened occasionally while during interval 3 the cleaning happened 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), and once additionally in September 2014.

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 July 2012 until January 2015 the sensor was successfully calibrated by the manufacturer as described in Fietzek et al. (2014). See table 1 for a summary of calibration conditions and results.

Table 1: Calibration identifier, dates, water temperatures, ranges as well as number of pCO₂ levels and values regarding the quality of the calibration polynomial fit (root mean square error, RMSE, and R²). Calibrations labelled 'a'/'b' are the pre- / post – deployment calibrations as used within data processing. Data were processed block-wise for each of these three deployment time intervals.

#	Date	Water temperature (T, °C)	Calibration range (pCO ₂ , µatm)	# pCO ₂ levels during calibration	RMSE (µatm)	R ²
1.a	10.07.2012	18 °C	200 – 3,000 µatm	7	5.28 µatm	0.999978
1.b	11.03.2013	18 °C	200 – 3,000 µatm	7	6.70 µatm	0.999964
2.a	25.03.2013	12 °C	200 – 3,000 µatm	7	5.04 µatm	0.999980
2.b	23.07.2013	17.5 °C	200 – 3,000 µatm	7	4.60 µatm	0.999983
3.a	14.11.2013	11.5 °C	200 – 3,000 µatm	7	8.89 µatm	0.999937
3.b	30.01.2015	11.5 °C	200 – 3,000 µatm	7	5.48 µatm	0.999973

Raw data were present in the form of multiple data files recorded by the manufacturer's software (CONTROS DETECT®) and/or 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 varied between deployments. Zeroings were e.g. carried out every 8 to 44 hours. A total of 22 files were finally used as the data input for further processing. The following processing steps were conducted:

1. Data preparation:

- a. Identical files in the datasets (artifacts from the computer-to-sensor-communication) were removed.
- b. All time stamps within the files were converted to UTC.
- c. Warm-up phases included in the data (not yet stabilized control temperature) were removed.
- d. Data from times of an uncoupled, clogged or turned-off underwater pump were removed through filtering for low pump current (within deployment interval 1 and 2) or pump power values (within deployment interval 3).
- e. During deployment interval 1, the NDIR sensor signal showed sporadic high outliers, which could be effectively removed through filtering of NDIR unit reference channel signal values. No such filtering was required for deployment intervals 2 and 3.
- f. Data was averaged into 5 min intervals to ease subsequent processing.

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-calibrations for the respective time intervals (tab. 1) as well as the information from the zeroing measurements.
- b. NDIR detectors overestimate CO₂ 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 of $\hat{\alpha}_v=1.62$ (Welles and McDermitt 2005).
- c. In case of data gaps between two zeroing events that were more than 24 hours apart, the course of the preceding or following 2 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. During deployment interval 3, there were periods with only one or two data points per zeroing. In first cases no zero values could be discarded and in the second case one of the two zero values was discarded during processing. This procedure made it necessary to manually remove 5 single zeroing outliers that deviated from the drift trend.
- e. In order to purge the data set from signal recovery periods (after preceding zeroings) more points were filtered. Data from this flushing period with a conservatively determined duration of 60 min were removed for the deployment interval 1 (partly a lower pump current/water flow in front of the membrane) and 30 min were removed for the deployment intervals 2 and 3. 15 not automatically detected signal recovery periods were manually removed during deployment interval 3.

3. Data finishing:

- a. Data were now averaged over 30 min intervals in order to reduce variability in the processed data due to different logging settings and sensor response times.
- b. Removal of an additional two deployment periods within the intervals (approx. 7 days in May 2013, approx. 4 days in July 2014) in which the sensor was deployed elsewhere.

In Fietzek et al. 2014 a deviation between HydroC[®] sensors and reference system data of $-0.6 \pm 3.0 \mu\text{atm}$ with an RMSE of $3.7 \mu\text{atm}$ was found resembling an estimated accuracy (RMSE) of approx. 1% from reading. **Despite the additional processing steps described above, we conservatively assume the accuracy of the $p\text{CO}_2$ data discussed here to be 5% of reading.** This assumption is based on the following observations:

- Deployment interval 1:
Variable pump speed (i.e. response time) and exceedance of the calibration range at some occasions.
- Deployment interval 2:
Variable pump speed (i.e. response time) and periods with internal pressures readings (i.e. within the gas stream behind the sensor's membrane) exceeding their measuring range.
- Deployment interval 3:
Hindered drift correction applicability due to deviant zeroing settings (i.e. duration and logging interval) and long time (>14 months) between pre- and post-calibration.

References:

- Fietzek, P., B. Fiedler, T. Steinhoff, and A. Körtzinger, 2014: In situ quality assessment of a novel underwater $p\text{CO}_2$ sensor based on membrane equilibration and NDIR spectrometry. *J. Atmos. Ocean. Technol.*, **31**, 181–196.
- Welles, J. M., and D. K. McDermitt, 2005: Measuring carbon dioxide in the atmosphere. *Micrometeorology Agric. Syst.*, 287–320.