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1 **In situ quality assessment of a novel underwater**
2 **$p\text{CO}_2$ sensor based on membrane equilibration**
3 **and NDIR spectrometry**

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Abstract

We present a detailed quality assessment of a novel underwater sensor for the measurement of CO₂ partial pressure (*p*CO₂) based on surface water field deployments carried out between 2008 and 2011. The commercially available sensor, which is based on membrane equilibration and NDIR spectrometry is small and can be integrated into mobile platforms. It is calibrated in water against a proven flow-through *p*CO₂ instrument within a custom-built calibration setup. The aspect of highest concern with respect to achievable data quality of the sensor is the compensation for signal drift inevitably connected to absorption measurements. We use three means to correct for drift effects: (i) a filter correlation or dual-beam setup, (ii) regular zero gas measurements realized automatically within the sensor and (iii) a zero-based transformation of two sensor calibrations flanking the time of sensor deployment.

Three sensors were tested against an underway *p*CO₂ system during two major research cruises providing an in situ temperature range from 7.4 to 30.1°C and *p*CO₂ values between 289 and 445 μatm. The average difference between sensor and reference *p*CO₂ was found to be $-0.6 \pm 3 \mu\text{atm}$ with a RMSE of 3.7 μatm.

33 1. Introduction

34 The measurement of dissolved carbon dioxide (CO_2) in seawater is important and
35 valuable for a large number of scientific, industrial as well as socio-economic issues.
36 Major scientific interest is related to the anthropogenic increase of atmospheric CO_2
37 concentrations and the resulting oceanic uptake of this most important anthropogenic
38 greenhouse gas (Sabine et al. 2004; Rogner et al. 2007). The exchange of CO_2 across the
39 air-sea interface and the dynamics and trends of the carbon cycle in coastal and open
40 ocean regions (Takahashi et al. 2009; Gruber et al. 2010) as well as in the interior ocean
41 are key aspects of current marine carbon cycle research.

42 Dissolved CO_2 reacts with water to form carbonic acid (H_2CO_3), which rapidly
43 dissociates into hydrogen (H^+), bicarbonate (HCO_3^-), and carbonate ions (CO_3^{2-}). The
44 exact speciation within the marine CO_2 system, i.e. between the above species of the
45 carbonic acid dissociation system, strongly affects the pH of seawater (Millero 2007) and
46 is of major interest. An increasing amount of dissolved CO_2 therefore leads to a
47 decreasing pH, a process also referred to as ocean acidification in the context of the
48 anthropogenic CO_2 transient. Its impact on calcifying organisms as well as on the
49 physiology and reproduction of other marine species is presently not well understood
50 (Doney et al. 2009). The potential long-term influence of acidification on fisheries but
51 also carbon capture and underwater storage scenarios (IPCC 2005) show the socio-
52 economic relevance of CO_2 measurements and highlight the demand for baseline
53 monitoring of CO_2 parameters in the ocean.

54 Since the thermodynamic constants of the marine carbonate systems are known
55 rather precisely (e.g., Millero 2007), the marine CO_2 system can be fully determined by

56 measurement of any two of the following variables: dissolved inorganic carbon (DIC),
57 total alkalinity (TA), pH and CO₂ fugacity ($f\text{CO}_2$) or CO₂ partial pressure ($p\text{CO}_2$; Millero
58 2007). Although the sole measurement of $p\text{CO}_2$ is not sufficient to fully characterize the
59 marine CO₂ system, $p\text{CO}_2$ is still a useful parameter on its own: It is the determining
60 factor for air-sea gas exchange and responds sensitively to biogeochemical processes
61 such as photosynthesis and respiration. Hence $p\text{CO}_2$ is both, a valuable stand-alone
62 measurement parameter and a useful measured variable within multi-parameter
63 measurements for the determination of the CO₂ system. So far only $p\text{CO}_2$ and pH can be
64 measured autonomously with commercial underwater sensors (DeGrandpre et al. 1995;
65 Seidel et al. 2008; Martz et al. 2010). Sensors for autonomous measurements of the other
66 carbonate system parameters TA and DIC (Byrne et al. 2002; Wang et al. 2007) and even
67 for direct measurements of carbonate ions are under development (Byrne and Yao 2008).

68 Due to a lack of a commercially available underwater $p\text{CO}_2$ sensor with a
69 sufficient accuracy and platform integratability expressed by adequate dimensions, an
70 appropriately short response time at surface and at depth as well as by the ability for
71 continuous measurements, we have advanced the development of an autonomous and
72 commercially produced underwater $p\text{CO}_2$ sensor (HydroC-CO₂, CONTROS GmbH, Kiel,
73 Germany). Its versatility and specifications allow for integration into various platforms
74 and provide a suitable tool for $p\text{CO}_2$ measurements at an improved spatial and temporal
75 resolution in the water column. Here, we present a comprehensive overview of the
76 sensor's measurement principle, its key components and its calibration. We also assess
77 the achievable data quality by means of a detailed analysis of data from surface water
78 field applications. Measurements against a proven flow-through system only represent

79 one application of the sensor, but at the same time enable the clearest assessment of the
80 sensors data quality. Many further applications in the water column are possible and best
81 require a dedicated discussions such as the measurements on a profiling float presented in
82 Fiedler et al. (2013).

83 *a. Suitable sensor platforms*

84 Beside classical mobile sensor platforms on the one hand, such as voluntary observing
85 ships (VOS) or research vessels, and stationary buoys and moorings on the other hand,
86 innovative mobile platforms are receiving growing interest (Fietzek et al. 2011). These
87 platforms, e.g. autonomous underwater vehicles (AUV), profiling floats and gliders,
88 provide an increased autonomy, mobility and versatility as opposed to the classical
89 carriers. They allow for a more cost-efficient data collection on so far largely unexplored
90 temporal and spatial scales. These newly accessible scales are of high interest for the
91 investigation of various biogeochemical processes, making these modern mobile
92 platforms desirable carriers for $p\text{CO}_2$ sensors (Gruber et al. 2010). By equipping
93 autonomous platforms as a regional or global sensor array with high spatiotemporal
94 resolution, such as the prominent Argo project, a high scientific potential can be achieved
95 (Roemmich et al. 2009; Johnson et al. 2009; Fiedler et al. 2013). However, in order to be
96 easily installed on modern mobile platforms, new sensors need to cope with the demands
97 of the more complex carriers and fulfill the more stringent requirements with respect to
98 payload capacity, power availability, response time, etc. A more detailed discussion of
99 these facts and circumstances can be found in Fietzek et al. (2011).

100 *b. pCO₂ measurements*

101 The first measurements of dissolved CO₂ were developed for medical applications in the
102 1950's. These were based on wet-chemical pH-determination behind a Teflon™
103 membrane (Stow et al. 1957; Severinghaus and Bradley 1958). Today optical CO₂
104 measuring techniques are prevailing. One method is to detect and quantify CO₂ molecules
105 within an equilibrated gas stream by means of direct absorption in the infra red (IR)
106 region of the electromagnetic spectrum. Another technique is an indirect measurement
107 making use of the pH affecting property of CO₂ by applying spectrophotometry within an
108 equilibrated pH-sensitive dye solution of known characteristics (DeGrandpre et al. 1995;
109 Lefèvre et al. 1993). An overview of current sensor techniques for carbonate system
110 species can be found in Byrne et al. (2010). A technical evaluation of pCO₂ sensors that
111 also includes two sensors of the type discussed here is presented in Tamburri et al.
112 (2011). Between the evaluation and the measurements discussed herein the status of the
113 sensors was mainly improved through an optimized calibration process and data
114 processing.

115 The usage of underway flow-through instruments to measure pCO₂ both in the
116 oceanic surface layer and in the atmosphere dates back to the 1960s (Takahashi 1961).
117 While in the beginning the application of these systems was restricted to research vessels,
118 current, improved systems are suitable also for application on unattended platforms such
119 as VOS (Watson et al. 2009; Pierrot et al. 2009; Pfeil et al. 2013). Continuous
120 optimization of the overall setup and the components used lead to some standardized
121 design that is nowadays also commercially available. The key components of such a
122 flow-through instrument are the air-seawater equilibrator and the IR gas analyzer. The

123 equilibrator is used to achieve partial pressure equilibrium between the dissolved gases in
124 a continuous stream of sea water and air that is re-circulated between the equilibrator and
125 a benchtop IR analyzer. The achievable measuring accuracy is 2 μatm for surface
126 seawater $p\text{CO}_2$ measurements (Pierrot et al. 2009). The flow-through system data are
127 commonly reported as $p\text{CO}_2$ although the $f\text{CO}_2$ is the value suggested for most accurate
128 carbonate system calculations. Based on approximated expressions the $f\text{CO}_2$, which
129 considers the slightly non-ideal behavior of CO_2 in the gas phase, can be calculated from
130 temperature and $p\text{CO}_2$, which presumes ideal gas behavior.

131 2. Sensor principle and description

132 *a. Development and design*

133 The development aims of the $p\text{CO}_2$ sensor among others were to obtain (i) a versatile and
134 autonomous sensor that could be deployed on a profiling float with (ii) a response time of
135 less than 5 min, (iii) an accuracy better 5 μatm , and (iv) a stability and reliability that
136 would allow for long-term deployments of several months.

137 Since the developed sensor is based on the same measuring principle as proven
138 flow-through systems, it has the same key components: an equilibrator and an IR CO_2
139 detector. A planar, semi-permeable membrane with a silicone active layer is installed in
140 the head of the sensor. It acts as an equilibrator as well as a phase separator between the
141 ambient water and an internal headspace. The sensor is commonly equipped with a water
142 pump that provides a continuous seawater flow to the membrane and thus reduces the
143 thickness of the static boundary layer in front of the membrane. By that, the response
144 time is effectively shortened and made independent of a relative movement between the

145 membrane and the surrounding water. In order to withstand high hydrostatic pressures the
146 membrane is mechanically supported from behind with a sintered metal disc. A gas pump
147 continuously circulates air between the membrane equilibrator and a non-dispersive IR
148 detector (NDIR). Figure 1 shows a model of the sensor and provides a schematic
149 overview of its setup. The gas tightness of the internal gas stream as well as of the
150 integrated valves is checked thoroughly prior to calibration. Opposed to $p\text{CO}_2$ underway
151 systems in which gas stream leakages are a major source for measuring errors (Pierrot et
152 al. 2009), the biggest “leak” within the gas stream of this sensor remains the equilibration
153 membrane; the high gas permeability of the membrane related to the volume of the gas
154 stream compensates for possible influences caused by small leaks. If bigger leakage
155 occurs within the gas stream, the entire, much larger internal gas volume of the sensor
156 will be equilibrated, leading to noticeably slower response times but not necessarily
157 biases. The gas circuit also features a specially developed gas heater upstream of the
158 NDIR detector whose heating control system is also used to stabilize the temperature of
159 the IR detector. The gas heater buffers seawater temperature gradients ($\Delta T_{\text{in-situ}}$) in such a
160 way that large $\Delta T_{\text{in-situ}}$ are damped to a much smaller gas temperature gradient. We
161 choose to set the control temperature just high enough for the heating control circuit to
162 keep the controlled temperature stable even at the maximum in situ temperature expected
163 during deployment. When the control temperature is set higher than necessary, avoidably
164 high power consumption is the consequence and the abundant absolute temperature
165 differences between the surrounding water and the internal gas becomes larger. In
166 addition to the gas heater and the temperature stabilization, the sensor’s pressure housing
167 is thermally insulated and temperature sensitive components are separately protected.

168 Within the gas stream sensors for pressure, temperature and relative humidity
169 (RH) are installed to determine the conditions within the NDIR detector as well as behind
170 the membrane. Their exact position was chosen upon laboratory tests to be most
171 beneficial for their consideration within the IR sensor data analysis. The quality and a
172 deep understanding of the NDIR detector are crucial for the data quality of both,
173 underway instruments as well as the new underwater sensor. All additional components
174 within the underway instrument's and the underwater sensor's gas circuit beside the
175 equilibrator and NDIR detector, such as the additional sensors mentioned above, are
176 required for accurate and precise absorption measurements and allow for preferably long
177 deployments.

178 In contrast to common practice of underway instruments the absorption
179 measurement within the sensor is carried out in wet air and without interrupting the gas
180 flow for measurement. In the underwater sensor regular zero gas measurements can be
181 carried out. Therefore valves are included into the circuit that lead the pumped air
182 through a soda lime cartridge instead of the membrane equilibrator at desired intervals
183 (see Fig. 1). In the presence of water vapor soda lime scrubs the CO₂ binding it as
184 calcium carbonate (CaCO₃) thus creating a zero gas with respect to CO₂.

185 The sensor operates by consecutively switching through different intervals, the
186 durations of which can be individually set. As soon as the sensor is powered it starts with
187 a warm-up interval followed by continuous repetition of measuring cycles. One
188 measuring cycle consists of three intervals: zero, flush and measure. The warm-up
189 interval is only passed through once after the sensor has been turned on. The required
190 warm-up time depends on the water temperature and the supplied voltage (c.f. Table 1).

191 During the warm-up, the water pump is disabled and data are neither transmitted nor
192 stored in the internal logger. During zero intervals, a zero CO₂ gas is created as described
193 above and the sensor provides the current zero reading used later for drift correction. The
194 zeroing typically lasts a few minutes and repetition is recommended at least every 12 h.
195 Data stored during that time are flagged for easy handling during analysis. Flush intervals
196 are only used to flag data acquired during the signal recovery from the zero value to the
197 ambient *p*CO₂ reading. Technically the measuring process of the sensor does not differ
198 between the flush and the subsequent measuring interval. The time the sensor needs for
199 full equilibration depends on the sensor configuration and the environmental conditions,
200 mainly the water temperature. The warmer the water, that faster the response time and
201 thus the shorter the required flush time. Laboratory and field tests for the response time
202 determination of the sensor as configured within the deployments presented here indicate
203 a linear dependency of response time on water temperature at a slope of the order of -1 s
204 per 1 °C (data not shown here). Sensor response to a step input can be well described by
205 first order kinetics and a corresponding exponential fit. Any response time given here
206 hence represents a time constant or a *t*_{63%} depending on which formulation is favored.
207 Isothermal pressure vessel experiments up to 200 bar have neither shown indications for a
208 pressure hysteresis, nor could a significant pressure influence on the response time be
209 identified (data not shown here). The actual response time of the sensor can be derived
210 based on the course of the signal recovery during the flush interval as applied by Fiedler
211 et al. (2013). It is typically faster than the 2 min response time of the flow-through system
212 (Pierrot et al. 2009) and allows for measurements on moving platforms; especially when
213 a response time correction is applied to derive the “true” ambient *p*CO₂ from the time-

214 lagged sensor signal (Fiedler et al. 2013). A more detailed analysis of the sensor's
215 response characteristics is in preparation. During flush and measurement intervals, the
216 water pump is active and data are recorded as configured. The interval settings simplify
217 the data processing and provide the means to generate measurement data from a fully
218 equilibrated and internally temperature stabilized sensor. Figure 2 shows the sensor signal
219 during calibration with the zero, flush and measurement intervals indicated.

220 The comparatively fast response time, small size and operability of the sensor
221 allow for deployments on various platforms. Due to its design and compared to classical
222 flow-through systems the maintenance intensity and the risk for leaks in the gas stream
223 are low. If used in situ, the sensor lacks the demand for an accurate water temperature
224 probe as it is crucial for typical flow-through systems (Körtzinger et al. 2000). In order to
225 derive the actual amount of dissolved CO₂ from the measured partial pressure, the sensor
226 is commonly deployed together with a CTD probe, as the solubility of CO₂ depends on
227 temperature and salinity (Weiss 1974).

228 *b. Specifications*

229 Table 1 lists the specifications of the developed sensor as applicable for the
230 measurements discussed in this work. Different data communication options are feasible.
231 An internal data logger is optional that can either be used as a stand-alone memory (e.g.
232 Saderne et al. 2013) or for backup storage (e.g. Fiedler et al. 2013). A sleep mode
233 function further facilitates autonomous installations. The sensor development also
234 comprised a surface water flow-through version of the sensor which is not further
235 addressed here.

236 *c. CO₂ measurements by means of NDIR spectrometry*

237 The properties of the NDIR detector are relevant for the overall performance of the
238 sensor. Drift, cross-sensitivities and the signal-to-noise ratio (S/N) of the NDIR detector
239 directly affect the data quality.

240 NDIR spectrometry in general is a proven direct measuring technique for mole
241 fractions of gases absorbing in the IR. It is non-destructive and traceable to standards.
242 NDIR detectors for CO₂ have small dimensions (several cm) and moderate power
243 consumption (here: about 0.5 W) that allow for easy integration. In addition they provide
244 good mechanical strength and are unaffected by vibrations if realized without moving
245 parts. Due to their high selectivity and limited cross sensitivity NDIR detectors are well
246 suited for qualitative analysis. NDIR detectors are composed of three main components:
247 light source, absorption/beam path and detector. Each of them has different influences on
248 the final sensor signal and depends differently on environmental variables, e.g.
249 temperature. This may lead to complex overall sensor properties. Their choice defines the
250 S/N, the sensitivity and the measurement range (detection limit and upper range value) of
251 an NDIR unit. The basic idea is to get enough light energy at the desired wavelength to
252 the detector and to make the absorption path sufficiently long such that changes in
253 absorbed light intensity can be clearly resolved by the detector and amplifying
254 electronics. Various options exist to optimize and dovetail these components.

255 The linear relation between the transmitted light intensity, I , and molecule
256 concentration, c , as described by the Beer–Lambert Law makes the technique suitable for
257 quantitative analysis:

258
$$I = I_0 10^{-\epsilon c l} , \quad (1)$$

259 with I_0 being the initial light intensity, l the distance the light travels through the
260 absorbing medium and ε the molar absorption or extinction coefficient of the target
261 molecule to be detected. According to (1) the extinction or absorbance, A , is defined to be
262 directly proportional to the molecule concentration in the medium:

$$263 \quad A = \log\left(\frac{I_0}{I}\right) = \varepsilon cl. \quad (2)$$

264 In reality there is a small non-linearity between the absorbance measured by the
265 NDIR detector and molecule concentration due to the fact that the Beer–Lambert law is
266 only defined for a single wavelength of infinitesimal small width, while in applications
267 spectral dependencies occur (Wiegleb et al. 2001).

268 The NDIR unit used features a black body radiator as a broad band IR light source
269 and a pyro-electrical IR detector which requires pulsed operation of the IR emitter.
270 Interference filters in front of the detectors select the desired measurement as well as
271 reference wavelength and together with electronics for control and evaluation complete
272 the single beam dual wavelength NDIR detector. CO₂ is typically sensed around 4.26 μm
273 where it shows its highest absorption due to its fundamental asymmetric stretching
274 vibration (2349.1 cm^{-1}) and the reference wavelength is chosen to be placed in the water
275 vapor window at around 4.0 μm .

276 Within an NDIR detector, several temperature influences exist that either require
277 a compensation, calibration or stabilization. The spectral properties of the filters are
278 temperature dependent: The central filter wavelength can shift as well as the transmission
279 width can vary. A temperature influence on the sensor can occur in the form of thermal
280 noise, a thermal background signal and changes in sensitivity. In the case of a dual beam
281 setup the influences might even be different for both channels. The emission properties

282 and emitted intensities of the light source show a temperature influence as well. Thermal
283 expansion of the cuvette or other mechanical deformations of the absorption path may
284 have an additional effect on the measurements. Finally temperature dependencies of the
285 analog electrical components directly behind the detector need to be considered. The
286 overall effect caused by temperature changes is hence both variable in magnitude and
287 sign for measurement channels of two similar products as well as for a measurement and
288 reference channel within the same instrument with separate filters, detectors and
289 electronics. For this reason and in order to enhance the measurement quality, the entire
290 NDIR detector is temperature stabilized within the sensor. An active temperature
291 stabilization furthermore helps to reduce the required warm-up time present in any NDIR
292 detector due to self heating effects. A separation of the light source and the detector from
293 the gas stream by windows enhances the temperature stabilization capability and protects
294 the sensitive detector with the filter. A gas heater further reduces the temperature gradient
295 within the cuvette and simultaneously reduces the risk of condensation within the optical
296 components of the sensor.

297 Any sensor based on an absorption principle such as an NDIR detector senses the
298 highest raw signal in the case of a complete absence of the target molecules in the beam
299 path as in that case no absorption occurs and the maximum radiation intensity reaches the
300 detector (see (1)). Therefore the regular determination of the sensor signal of a zero gas,
301 the *zeroing*, is essential to account for drift effects that alter the light intensity with time
302 and that otherwise would be erroneously interpreted as changes in target gas
303 concentration. Typical effects are:

304 (i) Intensity variations or spectral shifts of the light source over time,

- 305 (ii) Contamination of any component within the beam path that might cause
306 shadowing or growing reflectivity losses in the cuvette,
307 (iii) Aging effects that alter the detector sensitivity over time,
308 (iv) Changes in the pre-amplifier gain of the detector.

309 Within the sensor the zeroing does not only account for long-term drift influences
310 but also for changes of the measurement conditions such as large changes in water
311 temperature that cause internal temperature gradients and different water vapor
312 concentrations within the gas stream.

313 Drift compensation by means of a differential setup in our case realized in the
314 form of filter correlation is referred to as a two-beam/two-wavelength method. It is
315 supposed to compensate any unwanted influences that cause signal drift of both channels
316 in the same manner (aspects (i) and (ii) above) as the measured signal is continuously
317 referenced. Any effects that cause changes in the detector signals and that are not caused
318 by actual concentration changes within the cuvette shall be compensated in real time and
319 parallel to measurements. In reality, this technique has its limitations in accounting for
320 influences resulting from the usage of the two different channels with their own filters
321 and detectors. Theoretically the zero-point of a two-beam instrument should not be
322 affected by the above mentioned drift reasons ((i) through (iv)). But as we measure at two
323 different wavelengths, spectral differences as well as effects related to the two physically
324 different detectors still affect the zero signal of the “two-beam corrected” signal.
325 Therefore we combine the zeroing and the two-beam drift correction means within our
326 sensor. The latter provides a continuous correction applied parallel to measurements,
327 while the zeroing discontinuously further enhances the drift correction capabilities by

328 correcting for effects that differently affect the measured intensities at both detectors.
329 Related to the origin of NDIR detector drift in combination with the dual wavelength
330 setup it should be pointed out that changes in the zero concentration measurements can
331 (i) occur erratically especially after transportation or storage, (ii) are not necessarily linear
332 in time with (iii) the slope commonly decreasing over running time or (iv) even changing
333 its sign.

334 The zero correction of a two-beam sensor signal does not cover concentration
335 dependent effects that equate to changes in the characteristics of the NDIR sensor's
336 calibration polynomial. Hence for achieving best accuracies particularly with two-beam
337 NDIR sensors, the sensor in addition to regular zeroings needs to be re-calibrated after
338 deployment at different concentrations.

339 *d. Membrane equilibration*

340 The solution-diffusion model can be used to describe gas transport through a dense, semi-
341 permeable membrane. Assuming a partial pressure gradient between the water phase and
342 the internal gas stream, the first step within the transport process is adsorption of the
343 molecule at the membrane surface. In the case of a sufficiently small gas concentration
344 the dissolution process into the membrane can be explained by the Henry-Dalton Law,
345 which states the linearity between the partial pressure of a gas and the concentration of
346 that gas in solution connected by a temperature, pressure and, in the case of sea water,
347 salinity dependent constant. The dissolution process is followed by diffusion based
348 transport of the molecules within the membrane along the concentration gradient.
349 Outgasing into the headspace again follows the Henry-Dalton Law. This process
350 continues within the membrane of the sensor until partial pressure equilibrium with

351 respect to every single gas component is achieved. Hence semi-permeable membranes
352 can be used as equilibrators for dissolved gas measurements (McNeil et al. 2006). They
353 enable the application of gas phase based measuring techniques in an aquatic medium.
354 The time limiting and overall response time dominating step within the entire transport
355 process is the diffusion within the membrane material as well as within a boundary layer
356 in front of the membrane. The permeability of a material is a parameter integrating both,
357 the solubility of a gas within the membrane substance as well as its diffusion constant
358 within the membrane according to Fick's Law. Like the solubility and the diffusion
359 coefficient, the permeability is also temperature and pressure dependent as well as
360 concentration independent. The permeabilities of different gases for a given membrane
361 material differ (Robb 1968; Merkel et al. 2000) and hence determine the time constant for
362 the corresponding partial pressure equilibration. The direction of the transport process is
363 defined by the orientation of the individual partial pressure gradient. Silicone,
364 polydimethylsiloxane (PDMS), was chosen as the membrane material due to its high
365 permeability for CO₂ (Merkel et al. 2000).

366 In addition to all the dissolved gases, water vapor also permeates through the
367 membrane. Its amount within the gas stream is related to the temperature and salinity
368 driven water vapor pressure. The risk of condensation within the headspace and
369 especially within the NDIR absorption path induced by steep gradients of warm to cold
370 water is minimized by the heating of the gas on its way to the NDIR detector.
371 Furthermore the permeability of water vapor is more than a magnitude higher than for
372 CO₂ (Robb 1968), leading to time constants for water vapor equilibration of about 10 s at
373 the given CO₂ response time of about 70 s for this sensor.

374 Typically silicone layer thicknesses of around 10 μm are used. The thickness is
375 determined during membrane production by permeability measurements. Pure silicone
376 monolayer membranes of this thickness could not be easily handled. Therefore we use
377 thin film composite membranes consisting of the dense silicone layer on top of
378 supporting substructures. In the case of no or minor fouling the membranes can be
379 deployed for several months to years. Cleaning of the membranes with e.g. diluted
380 sulfuric or oxalic acid at pH 2 has successfully been tested. To avoid physical damage of
381 the thin silicone layer mechanical cleaning of the membrane surface should be avoided.
382 Instead the membrane should and can be changed even in the field. The response time of
383 the sensor determined from the flush interval data can also be used to identify organic
384 ongrowth, since heavy fouling slows down the membrane permeation process or the
385 volume rate of pumped water, which both leads to a reduced response time of the sensor.

386 3. In-water calibration setup

387 Along with the sensor development we established a laboratory calibration setup for
388 direct underwater $p\text{CO}_2$ calibration (Fig. 3) that can hold up to three sensors
389 simultaneously. An early version of the setup was successfully used in Friedrichs et al.
390 (2010). The setup includes a 120 L insulated and temperature stabilized water tank. The
391 water temperature can be controlled over the temperature range of 0°C to 30°C to within
392 $\pm 0.02^\circ\text{C}$. It is filled with de-ionized water. Sodium carbonate and bicarbonate are added
393 in the required quantities in order to mimic the CO_2 buffer system of seawater (DIC:TA
394 ratio) and thereby allow for a better $p\text{CO}_2$ level control. Silver nitrate is added as an anti-
395 foulant. Water is continuously pumped through a reference flow-through $p\text{CO}_2$ system
396 (Körtzinger et al. 1996), which was slightly modified to suit the laboratory conditions.

397 Additionally it was equipped with drying components to facilitate continuous reference
398 measurements in dry gas. Special care was taken that the return flow of the water from
399 the combined bubble-type/laminar-flow equilibrator into the main tank occurs without
400 flow restrictions and thus without altering the pressure conditions within the equilibrator.
401 Temperature probes within the equilibrator and the main tank are regularly calibrated
402 against a reference probe with an accuracy of ± 0.02 °C. The flow-through system is
403 equipped with a bench top IR analyzer (LI-6262 or LI-7000, LI-COR Inc, Lincoln,
404 Nebraska, USA), which is calibrated against 3 primary (certified National Oceanic and
405 Atmospheric Administration (NOAA) standards) or secondary (referenced to NOAA
406 standards) CO₂-in-natural-air standards in the beginning and in the end of each
407 calibration run. Processing of the flow-through system data is carried out according to the
408 procedures described in Dickson et al. (2007) and Pierrot et al. (2009), leading to $p\text{CO}_2$
409 reference values referred to the water temperature in the tank with an accuracy of 2-
410 3 μatm . During a full calibration run, the $p\text{CO}_2$ of the tank water is altered by pH
411 variation through injection of NaOH or HCl solutions. A new concentration in the tank
412 water is set and resolved by the reference system with a time constant of approx. 150 s.
413 By application of the pH-varying technique a wide $p\text{CO}_2$ -range can be realized and
414 calibration steps can be set as desired. Since the overall setup cannot be entirely
415 encapsulated from the surrounding air a small drift of the partial pressures in the tank of
416 typically around 3 $\mu\text{atm hr}^{-1}$ can be observed. Magnitude and timescale of this drift as
417 well as the fact that both, the flow-through system and the underwater sensor, detect this
418 $p\text{CO}_2$ change make this effect negligible with respect to the assumed accuracy of the
419 calibration process. The adjustable range is limited by the measurement range of the IR-

420 analyzer of the flow-through system, which is $3000 \mu\text{mol mol}^{-1}$ for the dry CO_2 mole
421 fraction in the equilibrated gas stream ($x\text{CO}_2$). It was found that four calibration steps are
422 sufficient for a sensor calibration in the range of 200 to 1000 μatm . The course of a
423 calibration is depicted in Fig. 2.

424 There are several reasons to calibrate the sensor in water against a proven
425 underway system as opposed to a mere dry gas calibration of the IR detector. The fact
426 that some of the following influences are already considered in data processing
427 corrections or their minimization was addressed in sensor design, does not debilitate the
428 following compensatory advantages of an in-water calibration. Firstly, the temperature
429 stabilization including the gas heater used in the sensor does not completely avert the
430 presence of temperature gradients within the instrument's housing, components and gas
431 stream. Hence the temperature stabilization can only minimize the above mentioned
432 possible temperature effects on NDIR sensors. An in-water calibration at a temperature as
433 close as possible to the expected temperature in the field helps to further reduce these
434 signal influences. Secondly, an in-water calibration as described compensates for all
435 effects related to the large absolute humidity present in the sensor's gas stream. These
436 effects are gas-gas-interactions causing band broadening, potential cross sensitivities of
437 the NDIR signal against H_2O due to minor H_2O absorption at the transmitted
438 wavelengths, or H_2O molecule interaction with the cuvette's surface. For a sensor
439 calibration at only one temperature it is deliberately accepted that the humidity related
440 compensations are only entirely compensated for a deployment at a water temperature
441 equal to the calibration temperature. Thirdly, an in-water calibration compares the fully
442 processed signal of the instrument with a reference value. Hence it characterizes the

443 overall instrument including the entire membrane equilibration process of the headspace
 444 as identified to be important by Byrne et al. (2010). Any not otherwise considered effects
 445 occurring in the sensor's gas stream and behind the membrane are taken care of by an in-
 446 water calibration.

447 4. Data processing

448 The dual-beam NDIR detector provides two signals. The raw signal, S_{raw} , corresponds to
 449 the transmitted light intensity around the wavelength at which CO_2 efficiently absorbs
 450 (4.26 μm) and the reference signal, S_{ref} , expresses the intensity at around 4 μm where
 451 practically no relevant absorption occurs. Water vapor is weak absorber at both
 452 wavelengths. A continuously referenced sensor signal, the “two-beam signal”, is:

$$S_{2\text{beam}} = \frac{S_{\text{raw}}}{S_{\text{ref}}}. \quad (3)$$

453 As a result of the regular zeroing (Z), we obtain “two-beam zero signals” at
 454 discrete points in time:

$$S_{2\text{beam,Z}} = \frac{S_{\text{raw,Z}}}{S_{\text{ref,Z}}}. \quad (4)$$

455 Linear interpolation in time between two adjacent $S_{2\text{beam,Z}}$ provides zero reference
 456 signals for every point in time: $S_{2\text{beam,Z}}(t)$.

457 An NDIR signal that is improved by both drift correction (DC) means, dual beam
 458 and zeroing, is derived as follows:

$$S_{\text{DC}}(t) = \frac{S_{2\text{beam}}(t)}{S_{2\text{beam,Z}}(t)} \quad (5)$$

459 The final, drift corrected NDIR signal, which is assumed to be directly
 460 proportional to the amount of target molecules in the beam path is related to $S_{\text{DC}}(t)$.

461 During calibration the flow-through system provides a reference $p\text{CO}_2$ for every
462 calibration step. The $p\text{CO}_2$ equilibrium is assumed to be established in the membrane
463 equilibrator of the sensor at that time. Using data of the peripheral sensors in the gas
464 stream, the $x\text{CO}_2$ in moist air present at the NDIR detector is derived. As the NDIR signal
465 is proportional to the number of molecules in the beam path and not to $x\text{CO}_2$, the
466 reference $x\text{CO}_2$ needs to be density corrected by using data of the additional temperature
467 and pressure sensors built into the gas stream of the $p\text{CO}_2$ sensor. A polynomial of rank 3
468 with a forced zero crossing is then used to calibrate the individual sensor characteristics.
469 It correlates the absorbance signal of the NDIR detector with the corresponding and
470 density corrected $x\text{CO}_2$ in the gas stream (c.f. Fig. 4). Now, all required dependencies are
471 known and the sensor provides the $p\text{CO}_2$ based on the absorbance signal of its NDIR
472 detector in combination with the data of the peripheral sensors in its gas stream. Beside
473 the density correction no other NDIR signal correction addressing a band broadening
474 effect as a consequence of $\text{CO}_2\text{-H}_2\text{O}$ molecule interactions or any other H_2O cross
475 sensitivity is explicitly included in the sensor sided data processing at this point. These
476 aspects are considered through the in-water calibration as mentioned in section 3.

477 Since the consideration of the zeroings requires an interpolation in time, this
478 calculation step is best applied during post processing of field data to obtain a smooth
479 behavior. In order to achieve the best measurement accuracy, changes in the sensor
480 characteristics should also be included into the processing. Therefore an interpolation
481 between the polynomial of a pre-deployment calibration and the polynomial of a post-
482 deployment calibration over the course of the deployment is conducted. We apply an
483 interpolation that is not linear with time, but instead linear with the actual value of the

484 zero signal throughout a deployment, $S_{2\text{beam},Z}(t)$. The pre-deployment polynomial is
485 transformed to the post-deployment polynomial by proportionately using the coefficients
486 of the two polynomials according to the actual zero signal. This approach assumes a
487 causal relationship between the temporally often non-linear change in the zero signal and
488 the change in concentration dependent sensor response.

489 The entire calibration calculations as well as the post processing are accomplished
490 with custom-designed LabVIEW routines (National Instruments, Austin, Texas).

491 5. Field evaluation

492 Field evaluations of the new $p\text{CO}_2$ sensor were carried out in April/May 2010 during a 6-
493 week cruise in the North and South Atlantic (R/V *Polarstern*, ANT-XXVI/4) and in
494 June/July 2011 during a 4-week cruise in the eastern tropical Atlantic (R/V *Maria S.*
495 *Merian*, MSM-18/3; Fig. 5). During these cruises, oligotrophic (i.e., subtropical gyres) as
496 well as mesotrophic regions (e.g., continental shelves, equatorial upwelling) provided a
497 reasonably wide range in $p\text{CO}_2$ (295 to 430 μatm ; c.f. Fig 6. and Fig 7. top panel) and
498 temperature (7.4 to 30.3°C, Fig. 5). Furthermore, strong $p\text{CO}_2$ and temperature gradients
499 were found near hydrographic fronts. Thus, the conditions were ideal for a thorough
500 evaluation of the sensor, which was tested during both cruises in nearly identical
501 underway setups: Seawater, either supplied by the ship's clean seawater supply systems
502 (ANT-XXVI/4) or by a submersible pump installed in the moon pool near the ship's keel
503 (MSM-18/3), was pumped to the laboratory into a thermally insulated flow-through box
504 (80 L volume) at a flow rate of approx. 12 L min^{-1} . Sea surface temperature (SST) and
505 sea surface salinity (SSS) were determined for both cruises at the seawater intake. A
506 sensor package containing the $p\text{CO}_2$ sensor (two units during ANT-XXVI/4, HC1 and

507 HC2; one unit on MSM-18/3, HC3) and an oxygen optode (Model 3830 or 4330,
508 Aanderaa Data Instruments AS, Bergen, Norway), which also provided the water
509 temperature in the flow-through box with an accuracy of $\pm 0.05^\circ\text{C}$, were placed in the
510 underway box. Data were binned into 1-min intervals. Since the $p\text{CO}_2$ sensor data were
511 initially stored at 5-s intervals the transformation to the 1-min intervals represents an
512 averaging of typically 12 spot values. Zeroings were carried out every 12 hours. The
513 membrane interface of the $p\text{CO}_2$ sensor was supplied with a constant seawater flow by a
514 SBE 5T pump (Sea-Bird Electronics Inc., Bellevue, Washington). A fully automated
515 $p\text{CO}_2$ underway instrument (GO, General Oceanics, Miami, USA; Pierrot et al. 2009)
516 based on a spray head equilibrator and a LI-7000 CO_2 analyzer was operated in parallel.
517 Throughout the expeditions and beside the deployment in the flow-through box the
518 sensors were additionally used for measurements on a CTD rosette system (HC1 and
519 HC3; part of the data shown in Fiedler et al. 2013) as well as on a surface drifter (HC3;
520 unpublished data).

521 The two sensors HC1 and HC2 were calibrated at 19.67°C before and after the
522 deployment. HC3 was pre- and post-calibrated at 27.00°C and 26.00°C , respectively.

523 The averaged sensor data were prepared for processing by filtering for obvious
524 outlier zero values as, for example, caused by improper sensor warm-ups, as well other
525 outliers and data biased through insufficient water supply to the flow-through box. All
526 $p\text{CO}_2$ sensor data recorded during flush and zero intervals were excluded from the
527 comparison with the reference. The data of HC2 obtained between 28th of April and 4th of
528 May were excluded from the comparison as well, as the excessively high water
529 temperature did not allow for temperature stabilization at the calibration control

530 temperature anymore. Although the control temperature within HC1 also temporarily
531 exceeded the set point, no data were removed here, as the unit seemed to be more robust
532 in this respect as compared to HC2.

533 Figures 6 and 7 show the $p\text{CO}_2$ measured by the flow-through reference system as
534 well as the $p\text{CO}_2$ data of the HC1-3 sensors with all datasets corrected to SST for direct
535 comparison (Takahashi et al. 1993). In addition, the $p\text{CO}_2$ differences ($\Delta p\text{CO}_2$) between
536 the sensor and the reference ($p\text{CO}_{2,\text{GO}}$) are plotted vs. time. The three $\Delta p\text{CO}_2$ curves for
537 every sensor are related to different drift compensation mechanisms:

- 538 (i) pre-calibration, no zeroings
- 539 (ii) pre-calibration + zeroings
- 540 (iii) pre-calibration + zeroings + post-calibration

541 In the case of (i) only the dual-beam correction is applied and the polynomial of
542 the pre-deployment calibration is used for the entire data set. Since in this case data are
543 processed by referencing all signals to the zeroing carried out during shore-based
544 calibration, large offsets can already occur at the beginning of a deployment due to a
545 sensor drift that occurred during storage and transport or due to measurement conditions
546 that strongly deviate from calibration conditions. Also more or less strong drift behavior
547 is observed over time. When the regular zero correction is carried out as described above
548 (section 4), both initial offsets and drift over the course of the deployment are strongly
549 reduced demonstrating the effectiveness of this first correction. However, even smaller
550 residuals were obtained when both zeroings as well as pre- and the post-deployment
551 calibration polynomials are considered in the post-processing (section 4). Table 2 shows
552 the statistics of the $p\text{CO}_2$ residuals as obtained by this optimized processing routine. In all

553 three sensor deployments the mean $p\text{CO}_2$ offset to the reference system is within
554 $\pm 3 \mu\text{atm}$. With an average $p\text{CO}_2$ residual over all three sensors of $-0.6 \pm 3.0 \mu\text{atm}$
555 (RMSE=3.7 μatm) no systematic offset between $p\text{CO}_2$ sensor and reference system could
556 be found. This indicates that the agreement between sensor and flow-through system
557 $p\text{CO}_2$ is of similar magnitude as the accuracy of the flow-through system which was
558 estimated at 2 μatm (Pierrot et al. 2009). We use the mean RMSE from all three
559 deployments of 3.7 μatm as a conservative estimate of the sensor accuracy. This result is
560 very promising as the sensors were only calibrated at a single water temperature and
561 experienced a large temperature range during deployment ($>20^\circ\text{C}$). We note that during
562 these field tests the sensors ran autonomously and without maintenance but were also
563 used in other tests (e.g., deployments of CTD rosette casts; part of the data shown in
564 Fiedler et al., 2013). For this purpose the instruments had to be restarted several times.
565 This appears to not have affected sensor performance negatively, since sensor HC3 was
566 restarted most frequently but shows the smallest overall offset.

567 The compensation routines applied, which exclusively rely on data measured by
568 the sensors themselves and the information obtained from calibrations, account well for
569 the signal drift for all 3 sensors. After processing the data do not exhibit significant
570 unaccounted drift behavior. This is even the case for the most strongly drifting sensor
571 HC1, whose signal change over time is also reflected by the change in its calibration
572 polynomials (Fig. 4). Although an NDIR detector drifting as strongly as in the case of
573 HC1 would not pass current quality controls within the manufacturer's production, it is
574 still a good example to demonstrate the effectiveness of the described processing
575 algorithms. We would like to note that sensor HC1 also participated in a different sensor

576 evaluation project (Tamburri et al. 2011). At that time, the sensor also showed a strong
577 drift that could not be adequately compensated for due to lack of the full understanding of
578 the required post-processing steps that is presented here. Although the drift of HC1 could
579 be well corrected for, in the end it still shows a slightly larger mean value and RMSE
580 compared to HC2 and HC3. NDIR detectors that show a smaller zero drift, typically
581 show a smaller concentration dependent signal change over time as well. This conclusion
582 is further corroborated by the observation that a transformation of the pre-deployment
583 into the post-deployment calibration polynomial based on the course of the zero values
584 finally provides a better correction as opposed to a transformation assumed to occur
585 linear in time (data not shown here).

586 In order to identify any remaining issues in the drift corrected $p\text{CO}_2$ sensor data,
587 the $\Delta p\text{CO}_2$ residuals were plotted against $p\text{CO}_{2,\text{GO}}$, SST and $p\text{H}_2\text{O}$ (Fig. 8). All sensors
588 show a weak correlation with all three parameters ($0.0 < R^2 < 0.6$), which is most clear for
589 sensor HC2 ($0.5 < R^2 < 0.6$). Since $p\text{CO}_{2,\text{GO}}$, SST and $p\text{H}_2\text{O}$ are strongly correlated in the
590 field data, the cause of these remaining residual correlations cannot be clearly discerned.
591 Nevertheless, there is indication for a weak NDIR signal dependency on $p\text{H}_2\text{O}$. In fact,
592 CO_2 -NDIR detectors over-estimate in the presence of water vapor due to pressure
593 broadening effects (McDermitt et al. 1993). Furthermore, the magnitude of this effect
594 increases with $p\text{CO}_2$ and $p\text{H}_2\text{O}$. Since the sensor calibrations were only conducted at one
595 temperature and band broadening effects due to varying water vapor concentrations are
596 not considered within the sensor's data processing, this might explain at least part of the
597 dependencies. The fact that HC2 and HC3 show the smallest $\Delta p\text{CO}_2$ around the water
598 temperature at which they were calibrated, support this observation. The limitations of

599 the present data set do not allow to further investigate this issue and additional tests have
600 to be carried out to assess the potential for further improvement, e.g., by performing
601 laboratory tests with and calibrations of the $p\text{CO}_2$ sensor at more than one temperature.

602 6. Summary and outlook

603 The development of a new underwater $p\text{CO}_2$ sensor based on membrane equilibration and
604 NDIR spectrometry was described. Special emphasis was put on compensation measures
605 for NDIR sensor drift as well as on the in-water calibration of the sensor. The
606 performance of the $p\text{CO}_2$ sensor was assessed based on surface water field data obtained
607 during two cruises both lasting at least one month and covering a wide range in $p\text{CO}_2$
608 (289 to 445 μatm) and temperature (7.4 to 30.1°C). A wet gas stream within a small
609 underwater sensor represents a demanding environment for NDIR detectors. Against this
610 background the observed mean offset of $-0.6 \pm 3.0 \mu\text{atm}$ with a RMSE of 3.7 μatm to the
611 $p\text{CO}_2$ reference instrument as obtained through application of a pre- and post-deployment
612 calibration in combination with regular zeroings is a very promising result, especially
613 since the sensors were also used for various other measurements including profiling
614 applications in the water column during the deployments (data not part of this
615 assessment). At a $p\text{CO}_2$ of 400 μatm the observed mean $p\text{CO}_2$ difference corresponds to
616 about 0.2 % and the RMSE to less than 1 %. This favorable result underlines the
617 efficiency of the applied processing algorithms. The acquisition of high-quality field data
618 by the new $p\text{CO}_2$ sensor calls for regular checks of the sensor parameters gas
619 temperature, pressure, RH and control temperature to guarantee optimal functioning of
620 the sensor. In addition, regular zero gas measurements need to be carried out at least
621 every 12 h under deployment conditions as a drift correction means beside the inherent

622 single-beam dual wavelength setup of the sensor. To properly apply the zero information
623 during post processing measurement data should always be flanked by zeroings. Thirdly,
624 in order to also account for the concentration dependant effects on zero and dual beam
625 corrected signals, the sensor needs to be re-calibrated at different $p\text{CO}_2$ levels on a time
626 scale of several months to a year to achieve the highest accuracies through data post
627 processing. A water calibration as presented in this paper at a temperature close to the
628 expected water temperatures in the field is beneficial. Nevertheless, the RMSE found
629 within this work is based on field data obtained under conditions where water
630 temperatures deviated by $\pm 10^\circ\text{C}$ from the calibration temperature.

631 The assessment given here represents an important milestone for the development
632 of the sensor. The procedures discussed are planned to be further automated and
633 implemented into data processing routines. The next development steps include
634 investigation of potential improvements with respect to NDIR data processing and the
635 laboratory calibration routines to identify and compensate for minor signal dependencies
636 on water vapor and on changes in gas matrix composition as caused by e.g. strongly
637 varying oxygen concentrations. Moreover the long-term stability during deployments on
638 moorings and profiling buoys in the water column will be investigated as well as the
639 sensor performance on different moving platforms analyzed. Especially the latter has
640 been simplified by a recently released smaller and faster version of the HydroC.
641

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770 **List of Figures**

771 TABLE 1. Specifications of the developed $p\text{CO}_2$ sensor as used during the deployments
772 discussed in this paper. The specifications of the currently available sensor model differ
773 from these values with respect to size and power consumption. The power required for
774 the temperature stabilization as well as the warm-up duration depend on the actual water
775 temperature, the chosen control temperature as well as on the thickness of the insulation
776 material. The given warm-up times correspond to 24 V supply voltage in 20°C water and
777 to 12 V supply voltage in 3°C water. Please refer to the text for further details regarding
778 the warm-up and the zeroing interval. The response times refer to the usage of two
779 different pump models at 20°C water temperature. The pump SBE 5T has a flow rate of
780 approx. 105 mL s^{-1} , while the smaller model, SBE 5M, provides a flow rate of approx.
781 35 mL s^{-1} .

782

783 TABLE 2. Statistics of the $\Delta p\text{CO}_2$ residuals for all three field deployments of the $p\text{CO}_2$
784 sensor with mean, standard deviation, σ , and root mean square error, RMSE, for a total of
785 n observations. Also shown is the mean of all three deployments.

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787 FIG. 1. Drawing of the $p\text{CO}_2$ sensor as used in the present study (upper panel). The sensor
788 is equipped with a water pump (SBE 5T) and a flow-head. The lower panel shows a
789 schematic drawing of the sensor. Partial pressure equilibration occurs at the planar, semi-
790 permeable membrane separating the water from the internal head space of approx. 20 mL.
791 A pump continuously circulates the gas between the membrane equilibrators, a heater and
792 the NDIR detector. Valves can be toggled to realize a zero gas measurement by guiding

793 the gas stream through a soda lime cartridge instead of through the membrane
794 equilibrator.

795

796 FIG. 2. Course of a calibration carried out at a constant water temperature within the
797 calibration setup described in the text. The absorbance NDIR signal shown in arbitrary
798 units is dual-beam and zero corrected. Also shown is the CO₂ mole fraction (x_{CO_2})
799 measured by the reference flow-through system. The numbers 1 – 4 indicate the
800 calibrations steps and “Z”, “F” and “M” mark the sensor intervals: zero, flush and
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802

803 FIG. 3. In-water $p\text{CO}_2$ sensor calibration setup. One water pump is used to allow for
804 sufficient mixing of the water in the tank, dispersion of the injected acid and base as well
805 as to provide water to the reference flow-through system, which is installed in a bypass
806 and whose NDIR unit is regularly calibrated with reference gases.

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808 FIG. 4. Calibration polynomials of sensor HC1 before and after the deployment on R/V
809 *Polarstern*. The absorbance NDIR signal is calibrated against the x_{CO_2} within the
810 sensor’s gas stream obtained according to the text. The polynomials match well the
811 sensor’s response characteristics (R^2 in both cases >0.999). A concentration dependent
812 change in the sensor characteristics between the different points in time (i.e., before and
813 after deployment) of the calibrations is clearly visible in this example for a strongly
814 drifting NDIR sensor.

815

816 FIG. 5. The cruise track of R/V *Polarstern* cruise ANT-XXVI/4 and of R/V *Maria S.*
817 *Merian* cruise MSM-18/3 (left) as well as the encountered sea surface salinity and
818 temperature (right panel). R/V *Polarstern* sailed from Germany to Chile and R/V *Maria*
819 *S. Merian* from Cape Verde to Gabon.

820

821 FIG. 6. $p\text{CO}_2$ data obtained by the GO-system as well as two HydroC sensors, HC1 and
822 HC2, during ANT-XXVI/4. The top panel shows the absolute values, while the middle
823 and bottom panel show the differences between the HydroC- $p\text{CO}_2$ and the reference
824 ($\Delta p\text{CO}_2$) over time for three different processing methods in order to visualize the
825 potential of different drift compensation mechanisms (refer to text). The black curve of
826 HC1 and HC2 represent the final drift corrected and post-processed signal. Refer to text
827 for further details on the different processing methods as well as on the peculiarities of
828 strongly drifting HC1.

829

830 FIG. 7. The $p\text{CO}_2$ trace during MSM-18/3 measured by the GO reference $p\text{CO}_2$ system,
831 and a HydroC sensor, HC3 (top panel). The lower panel shows the $p\text{CO}_2$ residuals
832 between the HydroC and the reference ($\Delta p\text{CO}_2$) for three different drift compensation
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837 SST (middle) and over the $p\text{H}_2\text{O}$ as measured within the internal gas stream close to the
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 852 approx. 105 mL s⁻¹, while the smaller model, SBE 5M, provides a flow rate of approx.
 853 35 mL s⁻¹.

Measurement principle	IR absorption measurement in a membrane equilibrated headspace
Detector	Single beam dual wavelength NDIR detector; zeroings at desired intervals
Housing, dimensions	Cylindrical titanium housing, 90 x 530 mm (without connector)
Depth capability	2000 m (standard)
Weight	5.5 kg in air, approx. 2.6 kg in water
Operating temperature	3 – 30°C
Supply voltage	11-24 VDC
Power requirements	<3 W for the detector and all the electronics, + <1 W – 3.5 W for temperature stabilization, + <6 W during warm-up for 2 – 30 min,

	+ 4 W during zeroing, + water pump: 7 W or 1.5 W (pump SBE 5T and 5M, respectively)
Sampling rate	≤ 1 Hz
Response time ($t_{63\%}$)	Approx. 70 s or 130 s (pump SBE 5T and 5M, respectively)
Measurement range	200 μatm – 1000 μatm (standard)

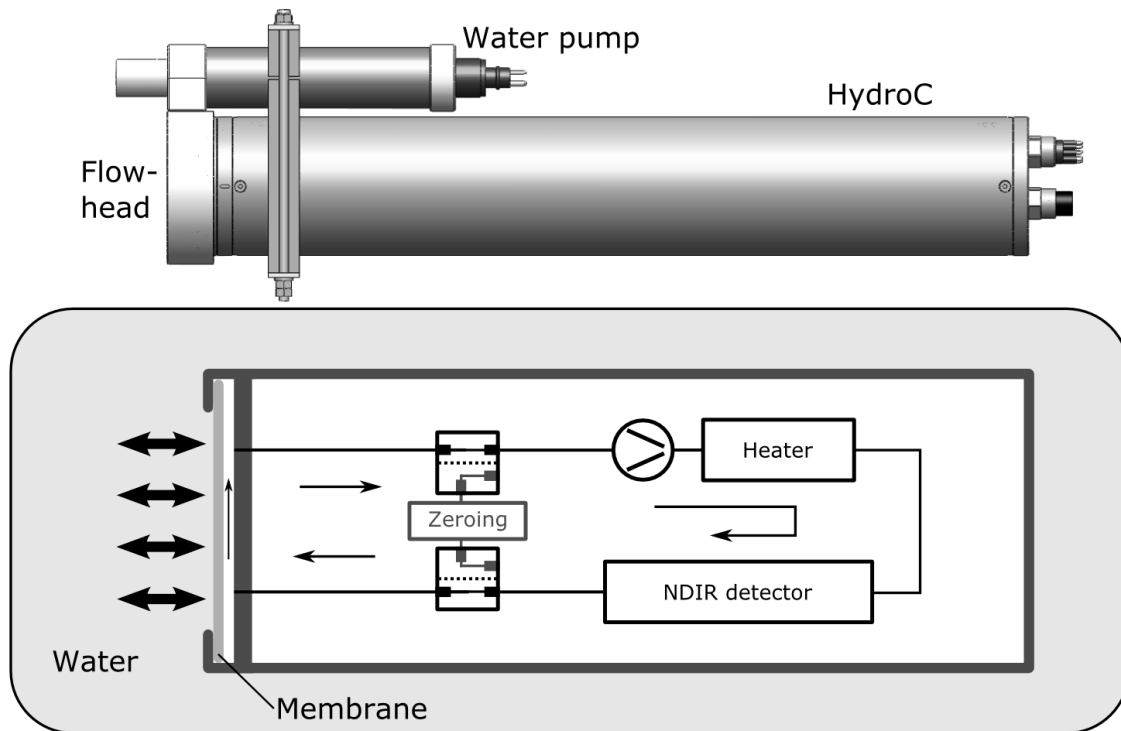
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856 sensor with mean, standard deviation, σ , and root mean square error, RMSE, for a total of
857 n observations. Also shown is the mean of all three deployments.

Sensor	Mean (μatm)	σ (μatm)	RMSE (μatm)	n
HC1	-3.1	2.9	4.2	24791
HC2	1.8	3.4	3.9	24163
HC3	-0.7	2.8	2.8	12770
Overall mean	-0.6	3.0	3.7	

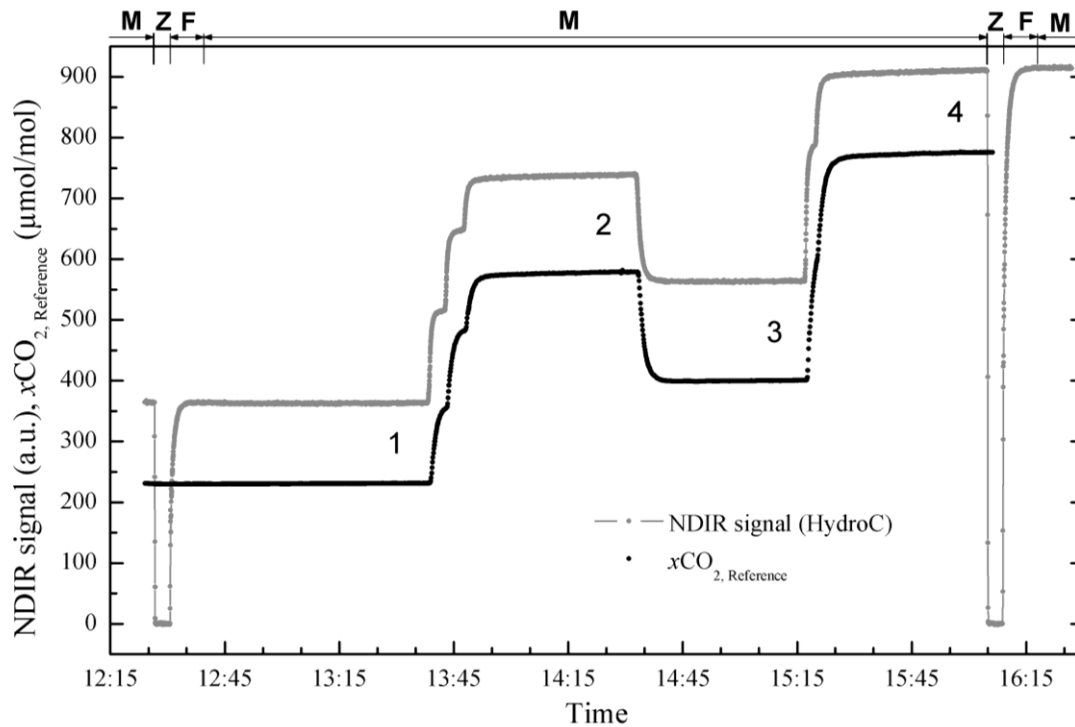
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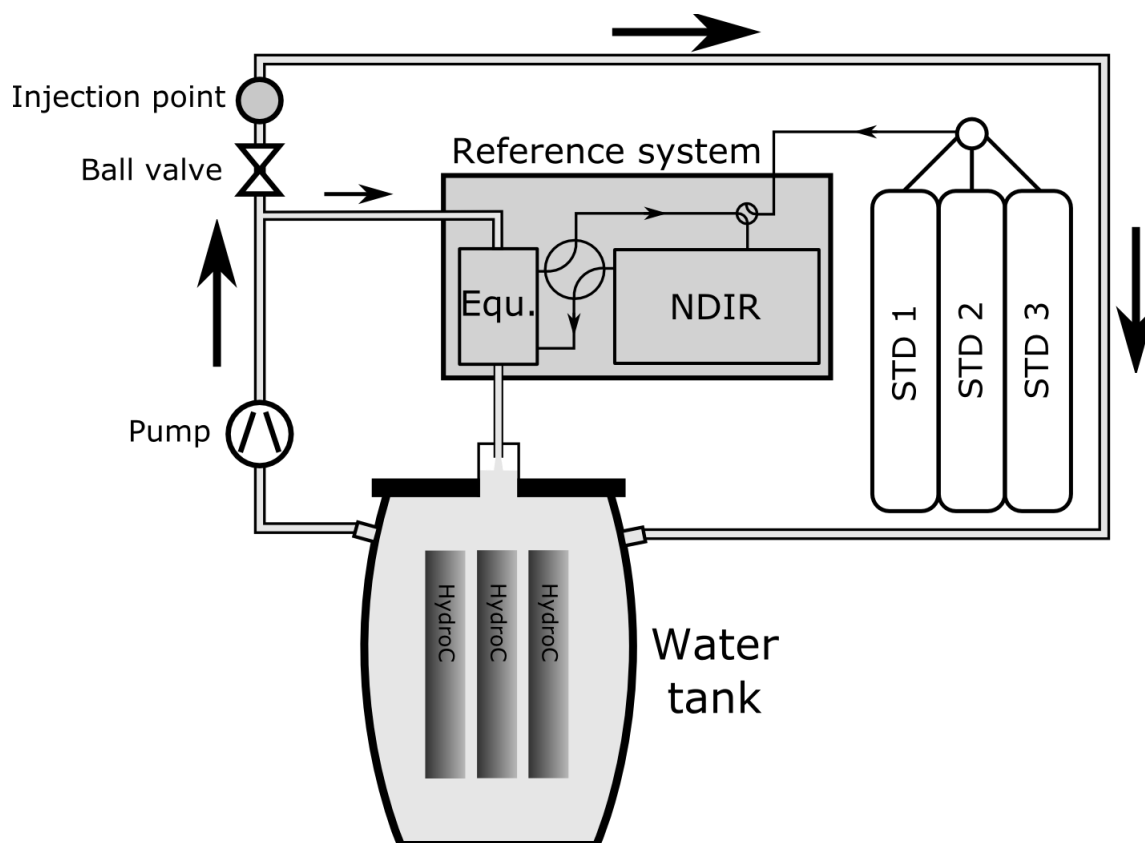
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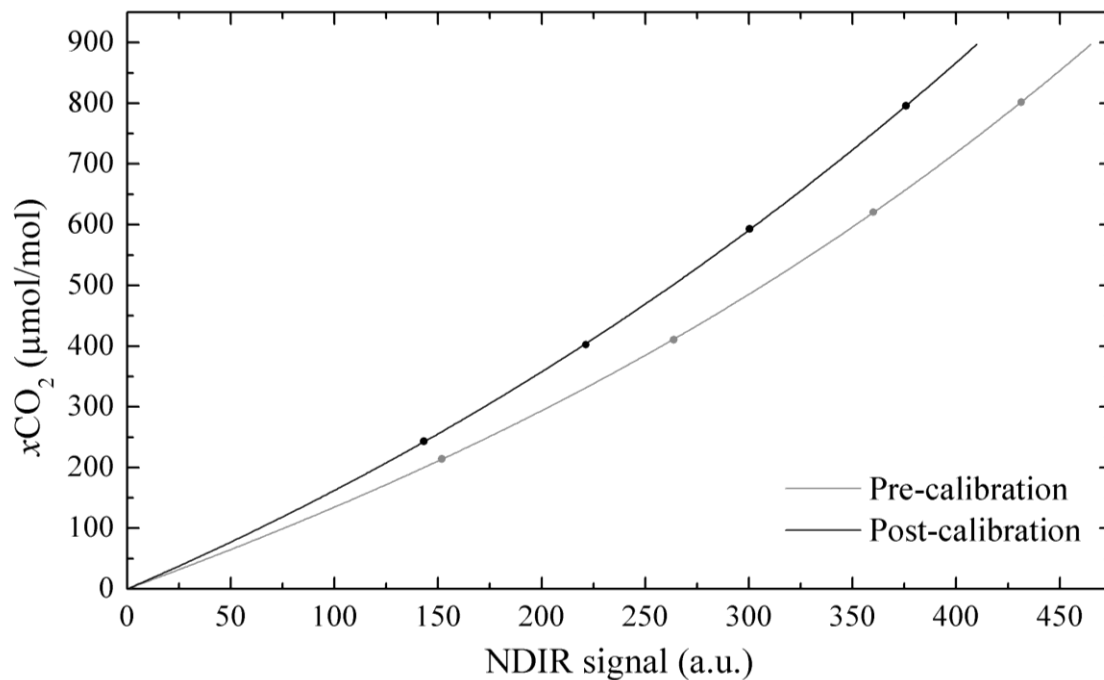
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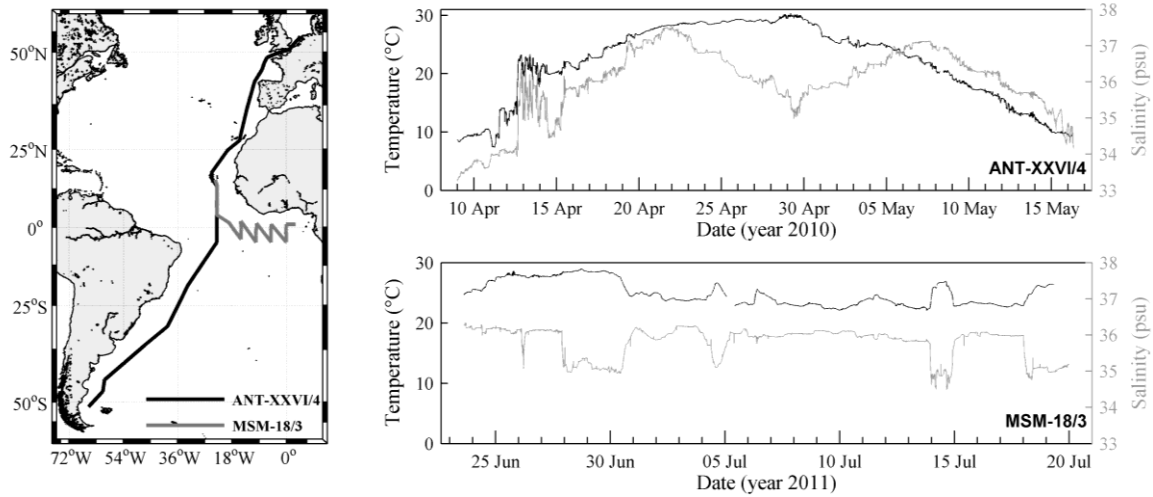
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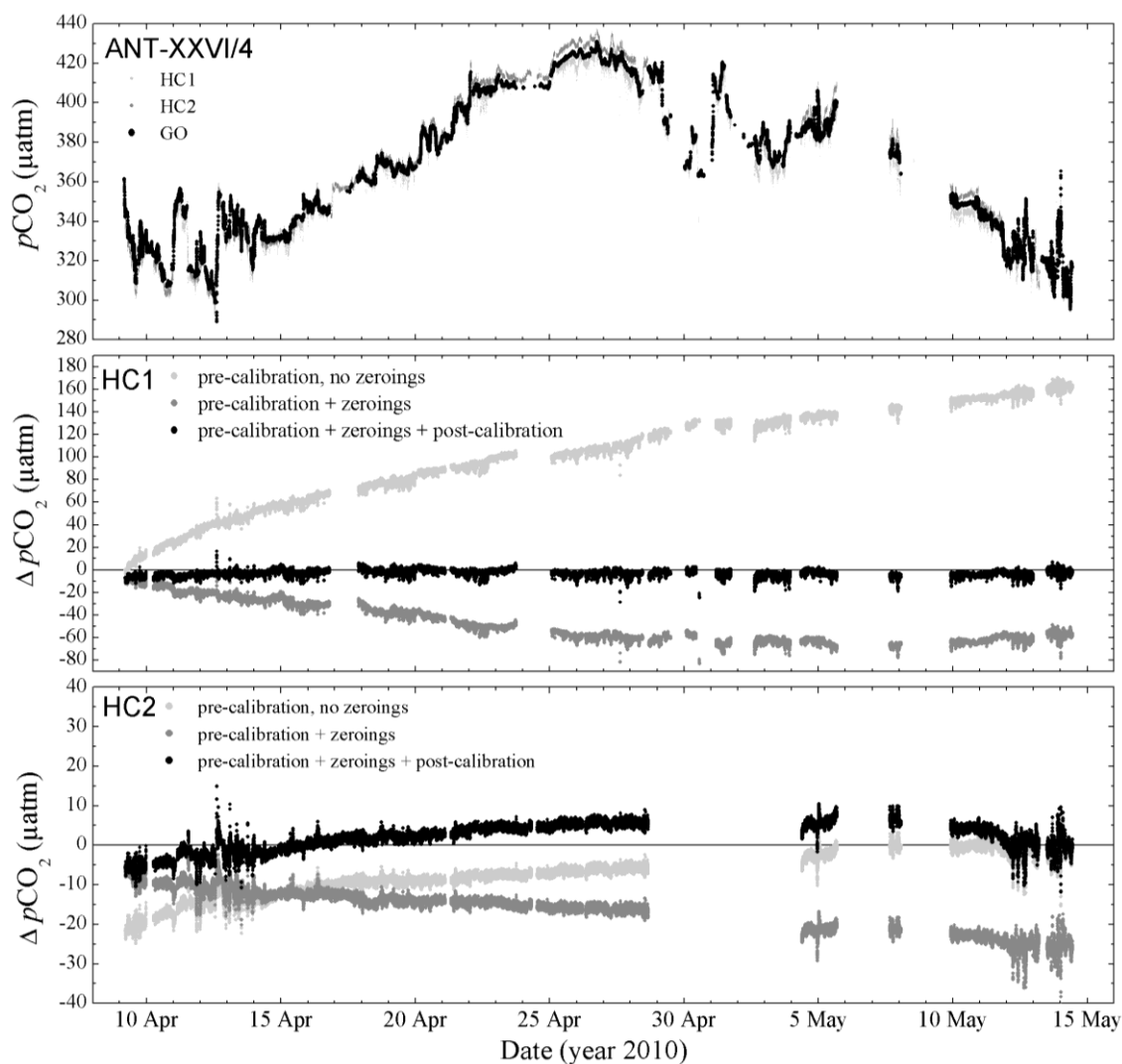
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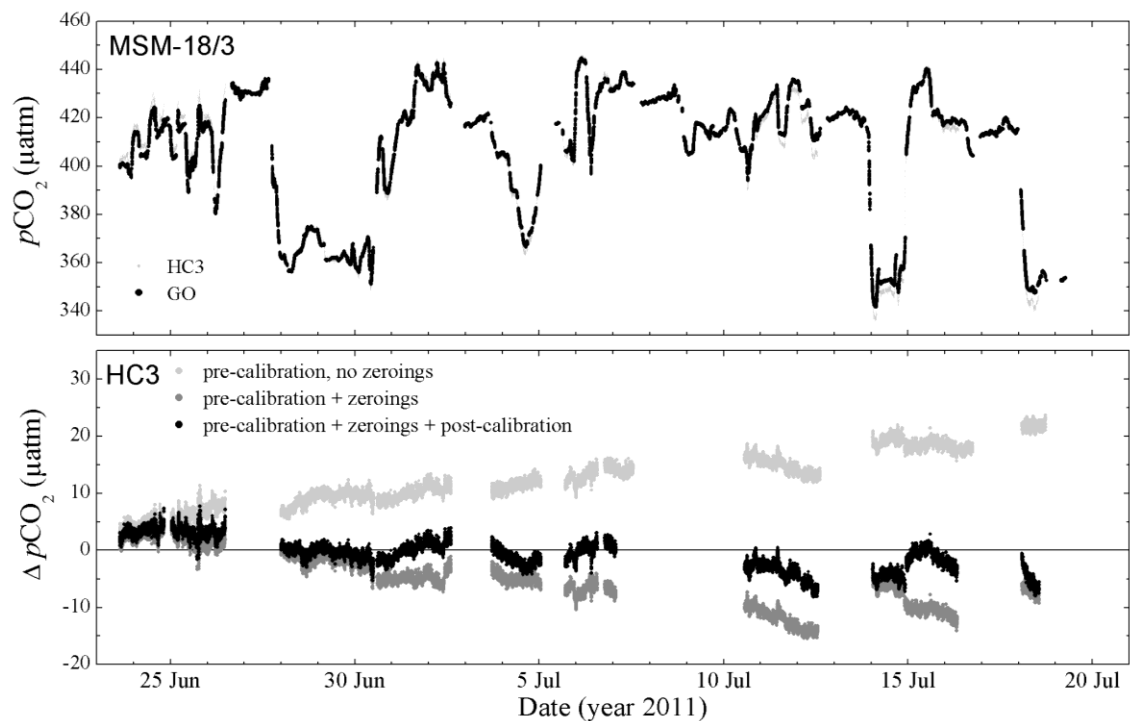


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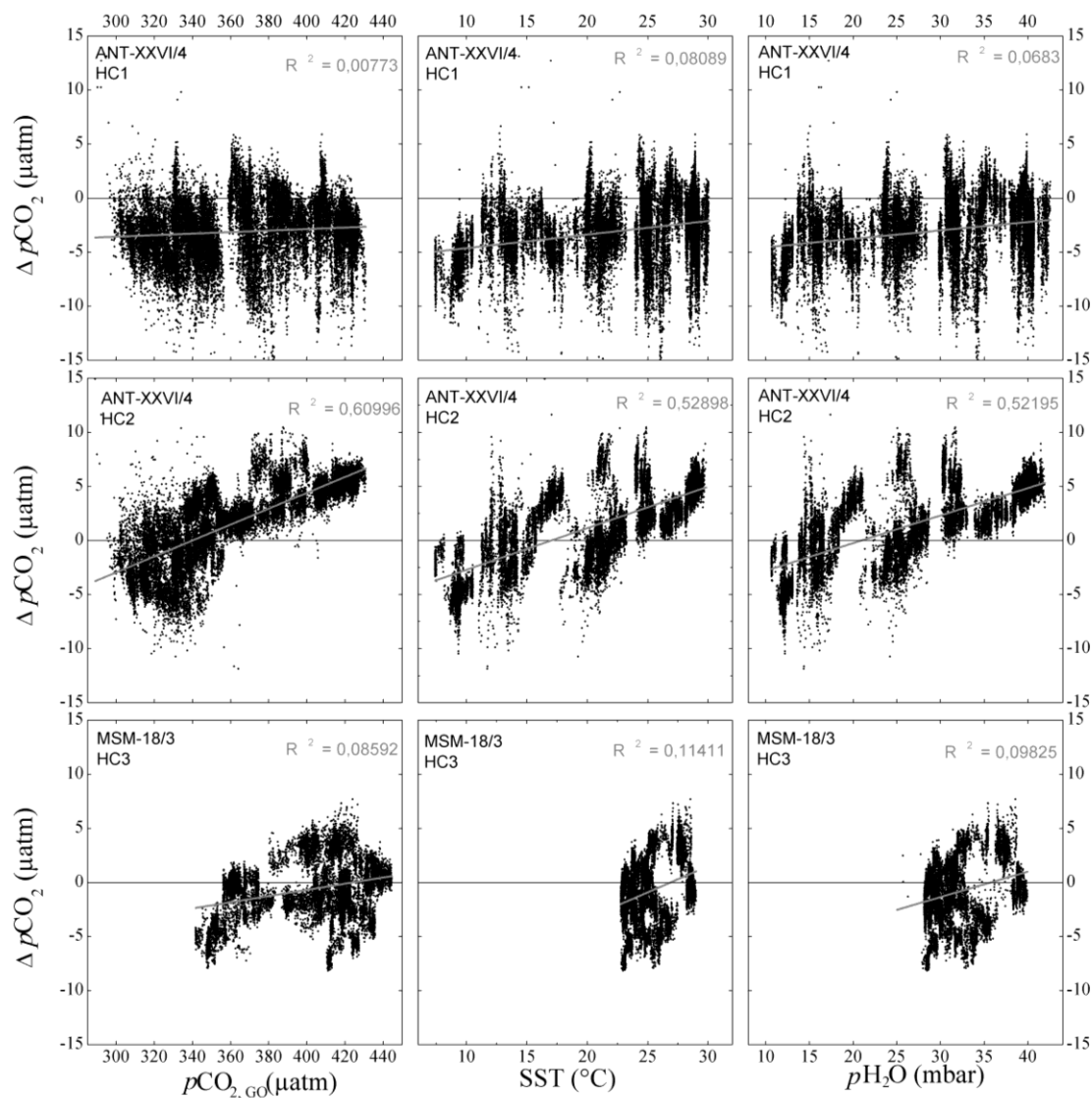
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