

Performance of a lifetime-based optode for measuring partial pressure of carbon dioxide in natural waters

Dariia Atamanchuk^{1*}, Anders Tengberg^{1,2}, Peter J. Thomas³, Jostein Hovdenes², Athanas Apostolidis⁴, Christian Huber⁴, and Per O.J. Hall¹

¹Department of Chemistry and Molecular Biology, Marine Chemistry, University of Gothenburg, SE-412 96 Gothenburg, Sweden

²Aanderaa Data Instruments AS, NO-5828 Bergen, Norway

³Christian Michelsen Research AS, NO-5892 Bergen, Norway

⁴PreSens GmbH, 93053 Regensburg, Germany

Abstract

This article reports the performance of an improved, newly developed, compact, low power, lifetime-based optical sensor (optode) for measuring partial pressure of dissolved CO₂ gas (pCO₂) in natural waters. The results suggest that after preconditioning, these sensors are stable in water for time periods longer than 7 months. The wide dynamic range of about 0-50000 µatm opens possibilities for numerous applications of which some are presented. In normal marine environments with pCO₂ levels of 200-1000 µatm, the best-obtained precision was about ±2 µatm, and the absolute accuracy was between 2-75 µatm, depending on the deployment and the quality of the collected reference water samples. One limitation is that these sensors will become irreversibly poisoned by H₂S and should thus not be deployed in sulphidic environments.

Carbon dioxide (CO₂) is a key substance involved in a number of biogeochemical processes in natural waters. The most common parameter, which describes the amount of dissolved CO₂ gas in water, is the partial pressure or pCO₂.

$$p\text{CO}_2 = P \times x(\text{CO}_2) \quad (1)$$

where $x(\text{CO}_2)$ = molar concentration of CO₂ gas in the dissolved gas mixture (usually air) and P = total pressure of gas mixture.

Together with dissolved inorganic carbon (DIC), total alkalinity (TA) and pH, pCO₂ determines and describes the carbonate system of seawater (see Sarmiento and Gruber 2006; Emerson and Hedges 2008). In aquaculture, especially in closed tanks, high pCO₂ levels are toxic to the animals, and

therefore, pCO₂ needs to be monitored and regulated. In connection with increasing atmospheric CO₂ levels, long-term pCO₂ time-series are essential to understanding if aquatic environments are sinks or sources of CO₂ (Wayne 2000; Takahashi et al. 2009; Bozec et al. 2011). Both large and small scale studies of pCO₂ on continental shelves, and in seas, rivers, lakes, fjords, bays, etc. are able to resolve major biogeochemical processes in the annual and interannual cycles (Thomas and Schneider 1999; Thomas et al. 2004; Kaltin and Anderson 2005; Wesslander et al. 2011). All of the applications described above require non-interrupted measurements, with a good temporal resolution to be able to understand the dynamics of the aquatic systems.

For aquatic in situ measurements of pCO₂, two different detection principles have been used: (1) infrared: based on the equilibration of the CO₂ gas dissolved in water through a gas-permeable membrane, with the inner air-filled compartment of the analyser, where the CO₂ concentration is measured optically using nondispersive infrared absorption spectrometry (HydroCTM/CO₂, CONTROS Systems & Solutions GmbH, www.contros.eu and CO₂-ProTM, PSI, www.pro-oceanus.com); (2) colorimetric: based on optical detection of the pH induced color change of the indicator solution, which is equilibrated with ambient seawater pCO₂ through a gas-permeable membrane (Goyet et al. 1992; DeGrandpre 1993; Lefèvre et al. 1993, DeGrandpre et al. 1995, SAMI pCO₂, www.sunburstsen-sors.com).

*Corresponding author: E-mail: dariia@chem.gu.se

Acknowledgments

This work was supported by SENSEnet, a Marie Curie Initial Training Network (ITN) funded by the European Commission Seventh Framework Programme under contract number PITN-GA-2009-237868. The installation and operation of the Koljo Fjord cabled observatory, which was used as a test site, were made in collaboration with Christoph Waldmann at MARUM, Germany, and funded by the EU-projects ESONET, HYPOX and EMSO. We acknowledge support from The Michelsen Centre for calibration and some test trials of the sensors.

DOI 10.4319/lom.2014.12.63

In recent independent field intercomparisons (Tamburri et al. 2011), these methods have demonstrated possibility to measure $p\text{CO}_2$ with good precision and accuracy. However, existing commercially available $p\text{CO}_2$ sensors are bulky and consume relatively high amounts of electrical power (3-10 W).

In this article, we describe and evaluate a compact, energy-efficient optical $p\text{CO}_2$ sensor designed for oceanographic applications. The performance of this type of sensor is evaluated in the laboratory and in different field applications. We highlight the importance of sensor foil preconditioning, as well as the effect of temperature and pressure. Interference, contamination, and cross sensitivity with other substances present in natural waters is described and tested. We also evaluate the long-term stability and field performance during several different in situ deployments.

Materials and procedures

Sensor description and measurement principle

Prototypes of optical $p\text{CO}_2$ sensors (model 4797, Fig. 1) from Aanderaa Data Instruments (www.aadi.no) were used in the present study. The mechanical design and the functioning of these sensors are similar to the oxygen optodes described in Tengberg et al. (2006). The sensor housing is made of titanium, rated to 600-bar pressure (1200 bar is optional), with a diameter of 36 mm and a total length of 86 mm. This housing includes an optical part, a temperature sensor placed close to the foil, and the necessary electronics (a microprocessor with digital signal processing capacity) to process signals and output absolute temperature compensated CO_2 readings (in μatm or mg/L concentration). As opposed to most other in situ CO_2 sensing systems, the power consumption of these sensors is

low and about 80 mW at 5-s sampling and 7 mW at 1 min sampling frequency.

The sensing foils were developed specifically for these sensors by PreSens (www.presens.de) and are composed of two fluorescence indicators embedded in an ion-impermeable, hydrophobic and gas permeable polymer layer that is coated onto a thin film of polyester or a glass support (Fig. 1). One of the indicators responds to changes in the surrounding pH by exhibiting a change in the intensity of blue light-induced fluorescence. In principle, the presence of this indicator is sufficient to detect CO_2 gas as it diffuses from the surrounding water into the sensing layer, modifying the pH. However fluorescence intensity measurements are susceptible to factors such as variations in the background light and excitation intensity. In this regard, fluorescence lifetime measurements are preferred. Therefore, the sensing foils used in our investigations incorporate a second 'reference' fluorescence indicator, whose fluorescence excitation and emission spectra overlap significantly with those of the first indicator, but whose fluorescence intensity is independent of pH. A further critical property of the reference indicator is that its fluorescence lifetime is longer relative to the lifetime of the pH indicator (μs compared to ns). When the combined indicators are excited with amplitude modulated blue light, each luminophore contributes an optical fluorescence signal that lags from excitation (Fig. 2), the longer fluorescence lifetime of the reference indicator means that the reference indicator φ_{ref} signal lag is larger than that of the pH indicator signal φ_{pH} . The combined intensity of the two fluorescence processes lags from the excitation signal by a phase φ_{DLR} . φ_{DLR} is associated with the fluorescence lifetime of the combined indicators. φ_{DLR} is depend-

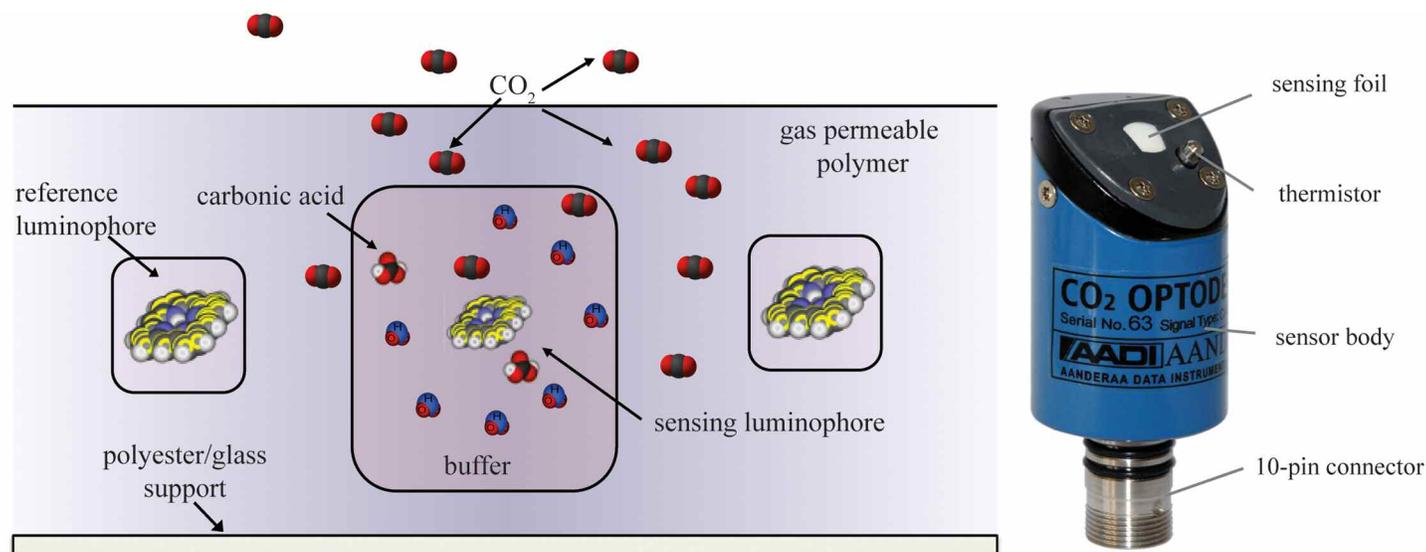


Fig. 1. Composition of sensing foil and an outside view of the evaluated 4797 $p\text{CO}_2$ sensor. Sensing foil (left) consists of DLR material, which is coated onto a thin film of polyester or glass support. The outside view of the sensor (right) shows location of the sensing foil and the nearby-situated thermistor on the sensor body. An internal processor translates the signal into a $p\text{CO}_2$ value and transmits it to a data recorder/instrument through a 10-pin connector.

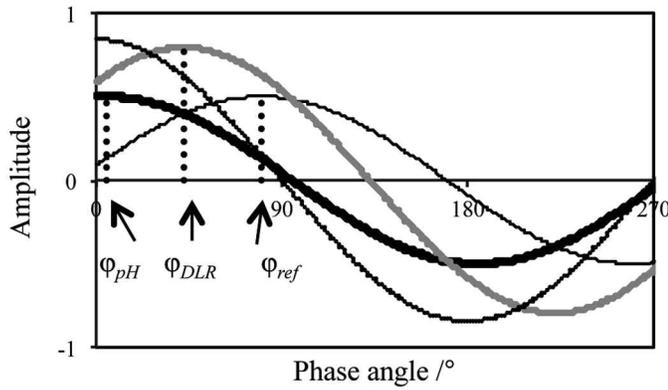


Fig. 2. The Dual Lifetime Referencing scheme: amplitude profiles for excitation light (dotted), fluorescence emission of the pH sensitive indicator (thick black), reference indicator (thin black), and the measured total fluorescence signal from the combined indicators (gray).

ent on the relative fluorescence intensities of the two dyes, but since only one of them has a fluorescent intensity dependent on pH, measurement of φ_{DLR} can be used to detect CO₂. The long fluorescence lifetime of the reference indicator also means that φ_{DLR} can be recorded using more power efficient lower speed (kHz) electronics. This measurement approach is known as Dual Lifetime Referencing (DLR) (Klimant et al. 2001; von Bültzingslöwen et al. 2002). The pCO₂ optode prototypes described in this investigation use 505 nm LED illumination for the excitation light. The fluorescence light is detected by a photodiode fitted with a long pass filter to exclude light from the excitation LED (Liesch et al. 2001).

The dependence of the phase shift (φ) value on pCO₂ can be described by an eighth-degree polynomial function, which fits for low pCO₂ in natural waters (0-10000 μ atm) and accounts for temperature changes (Eq. 2)

$$\log(\text{pCO}_2) = C_0 + C_1 \times \varphi + \dots + C_8 \times \varphi^8 \quad (2)$$

where $C_0 \dots C_8$ are temperature-dependent coefficients.

Calibration set-up and calculations of calibration model

For the calibration procedure, several sensors were immersed into a vessel containing 0.9% (9 ppt) NaCl water. Normally eight (or seven) different pCO₂ levels were obtained by using mass flow controllers to mix N₂ and CO₂ gas before being bubbled into the vessel through a diffusing element. Eq. 3 gives the partial pressure of CO₂ in the test fluid at equilibrium in hPa or mbar

$$\text{pCO}_2 = r(\text{p}_{\text{atm}} - \text{p}_w) \quad (3)$$

where $r = \frac{\dot{m}(\text{CO}_2)}{\dot{m}(\text{CO}_2) + \dot{m}(\text{N}_2)}$ and the \dot{m} are the gas mass flow rates. p_{atm} is the measured atmospheric pressure, whereas the vapor pressure of water (in hPa or mbar) is given by

$$\text{p}_w \sim e^{\left(\frac{A-B}{T} - C \ln T\right)}, \text{ where } A = 52.57, B = 6690.9, C = 4.681, \text{ and } T$$

is the temperature in Kelvin. The effects of hydrostatic pressure were not considered as the gas bubbles were introduced near the water surface. r was adjusted to cover a range of 0-10000 μ atm pCO₂.

The container was temperature controlled by using an immersion element and a heating/cooling circulator Julabo F12-EH. Five temperature regimes were usually used for the calibration: 0.5, 10, 20, 30, 40°C (accuracy $\pm 0.1^\circ\text{C}$). The gas mixture (N₂ + CO₂) was bubbled until saturation of the water and stable readings from the sensors were obtained at each temperature.

To cover the large dynamic range an eighth by third degree polynomial is used to produce a calibration model. In the curve-fitting algorithm, the calibration range is divided into three pCO₂ sections for each temperature. In each section $\log(\text{pCO}_2)$ is fitted to a third-degree polynomial. These curves are again, with some degree of overlap, fitted to the eighth degree polynomial. At last, a third-degree polynomial fit is applied to the coefficients of the eighth degree with respect to temperature. This method provides a continuous fitted surface and maintains a good control of the surface outside and in between calibration points in spite of the high-degree polynomial.

Simple one-point referencing is used to correct the calibration model if the sensor pCO₂ response is shifted. Reasons for such shifts are discussed later. The influence of the correction on the calibration surface is given in Fig. 3. Equation 4 shows how the corrected pCO₂ values are calculated based on existing calibration.

$$\log(\text{pCO}_2) = (C_0 + C_1 \times \varphi + \dots + C_8 \times \varphi^8) - \text{const} \quad (4)$$

where $\text{const} = \log(\text{pCO}_{2 \text{ ref}1}) - \log(\text{pCO}_{2 \text{ ref}0})$ or $\log(\text{pCO}_{2 \text{ ref}1}) = f(\varphi_1)$, $\log(\text{pCO}_{2 \text{ ref}0}) = f(\varphi_0)$. φ_1 is a measured phase shift, and φ_0 is a phase shift at given pCO₂ and T according to the existing calibration model.

Cross-sensitivity and poisoning

The solubility of the non-ideal CO₂ gas with respect to temperature, salinity, and pressure, which gives an estimation of pCO₂ and the absolute concentration of CO₂ in water, were comprehensively described by Weiss (1974) and Culbertson and Pytkowicz (1968).

Interference from substances present in natural waters was studied and evaluated both in field campaigns and in the laboratory. A common and expected interfering compound in natural waters, especially anoxic basins, is hydrogen sulphide (H₂S). An irreversible poisoning of the sensors by dissolved hydrogen sulphide gas was first observed in field campaigns in the Baltic Sea, and later underwent detailed investigation in the laboratory.

An H₂S stock solution was prepared. The 0.9% NaCl aqueous solution was bubbled by N₂ gas to get rid of dissolved oxygen in the water, which could change the H₂S concentration

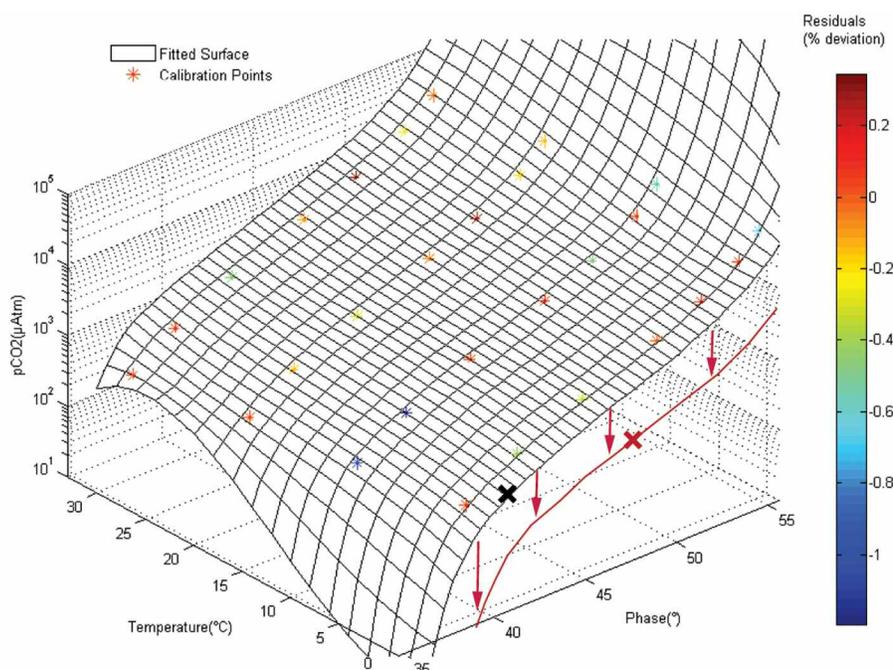


Fig. 3. The 3-D calibration surface shows a dependence of phase shift with respect to different pCO₂ levels at different temperatures. Stars represent actual measurements, and residuals are color-coded when compared with calibration model. A shift of the calibration surface in the direction of the red arrow illustrates the one-point referencing correction procedure: the red cross represents the reference measurement, the black cross is the corresponding pCO₂ value according to the original calibration. The surface is shifted down to align reference point to the calibration surface.

by oxidation. One pCO₂ optode was immersed in the solution under stirring. The concentration of H₂S was stepwise increased from 60 to 175 µmol/L H₂S (naturally occurring levels). After exposure to H₂S, the sensor was put into oxygenated seawater to examine the extent of poisoning. The data were recorded with 10-s intervals by using serial (RS-232) connection to a PC and a standard terminal program.

Foil preconditioning

Normally, this type of foils is used in biomedical applications where the salinity is constant at 0.9% NaCl (9 ppt). After production, the foils are stored wet at this salinity. In marine applications, the salinity is normally higher and more variable. To investigate if and how sensors are affected, we did several lab experiments. Two pCO₂ optodes were run in parallel and left to stabilize (precondition) in seawater for months in a thermo-regulated laboratory under identical conditions. The effects of changing temperature (15°-35°C) and salinity (17-33) were then investigated. The data were recorded at 10-s intervals to a PC in the same way as was described above.

Response time and pressure effects

Response time tests were conducted at different temperatures simply by moving an optode located in a water vessel with ambient pCO₂ (5000 µatm) to a vessel with 5% CO₂ concentration (50000 µatm), which is more than 50 times higher concentration than what is expected in natural waters.

A similar set-up as described in Tengberg et al. (2006) for controlled testing of oxygen optodes at different conditions,

including at high pressure, was used for parallel pressure testing of two pCO₂ optodes. The sensors were immersed into a stirred and pressure-compensated chamber filled with a solution of 0.9% NaCl with a pCO₂ of approximately 5000 µatm. The whole assembly was placed inside a pressure test chamber and subjected to hydrostatic pressures of up to 600-bar overpressure.

Long-term stability

Bleaching of the sensing films and/or drift in the electronics related to high frequency sampling can induce errors/drift in the measurements. To evaluate this a laboratory experiment was set up. Two pCO₂ optodes were placed side by side under identical conditions and set to measurements at different intervals for 1 month. The first sensor was collecting data at a fixed sampling interval of 30 seconds, summarizing a total of about 80000 excitations. The second sensor was measuring at a 30-s interval for 8 h/day, reaching an average of 500 excitations/day and a total of 16500 excitations.

Apart from bleaching, chemical changes in the composition of pCO₂ sensing foil could also influence sensor stability. Two pCO₂ sensors were compared in a laboratory stability test. One of the sensors was immersed and preconditioned in seawater (salinity 33) for 1 month before the experiment, while the other one was new and unused. During the stability experiment, which lasted for approximately 2 months, both pCO₂ sensors were kept under identical conditions in 0.9% NaCl solution at a temperature of 10°C and 1% CO₂ in a bubbling gas mixture. The data were recorded at 30-s intervals to a PC.

These pCO₂ optodes were used in several long-term (5-7 months) studies (Table 1). One long-term field stability experiment was done in the Koljo Fjord, Swedish west coast, for a time period of 7 months. In September 2011, one pCO₂ sensor was installed on a cabled observatory (EU projects ESONET, HYPOX and EMSO) at a water depth of 12.6 m in the Koljo Fjord. Back to back with this sensor, an AADI 4835 oxygen optode was installed. In addition, the observatory carries more than 30 other sensors measuring, e.g., oxygen, salinity, temperature, particles/turbidity, water level, and currents at different water depths in the fjord. The data are available online at <http://mkononets.dyndns-home.com:8080>. The sampling interval during the 7 months of measurements was 30 minutes. During the deployment, reference water samples were taken twice.

Other field applications

pCO₂ optodes were used on one of the autonomous Goteborg benthic landers during several expeditions to study mineralization processes, by doing sediment-water incubations, in situ at the sea floor. Examples of recent work with these instruments are given in Almroth et al. (2009), Almroth-Rosell (2012), and Viktorsson et al. (2012, 2013). In most of this fieldwork, four sensors were used in parallel. Two of them were placed inside the benthic chambers (Fig. 4), which also carried oxygen optodes and conductivity/salinity sensors, and two on the lander frame outside the chambers in the ambient bottom water. Oxygen decrease inside the chambers was compared with increasing levels of pCO₂. Data from these four and other sensors were logged by a Seaguard multisensor platform (www.aadi.no).

To evaluate if pCO₂ optodes could be useful tools in aquaculture applications to study e.g., CO₂ build-up in the tanks and stress levels of the fish, two sensors were mounted on a Seaguard platform that was deployed for 1 month in land-based salmon fish tanks.

Other field applications in which these sensors have been successfully used include the QICS project (<http://www.bgs.ac.uk/qics/home.html>), which is dealing with subsea geological CO₂ storage and the ability to detect leakage from a storage site. Data from the QICS work will not be presented in this article.

Reference data

Reference values for validating the performance of pCO₂ optodes were obtained from manual water sampling, with consecutive corresponding analysis and calculations. CO2SYS

software developed by Lewis and Wallace (1998) (<http://cdiac.ornl.gov/oceans/co2rprt.html>) uses any two of four (pCO₂, DIC, TA, pH) parameters of the carbonate system to calculate the other two. We used DIC and TA as the two input parameters. In the calculations, we also used a set of dissociation constants from Mehrbach et al. (1973) refitted by Dickson and Millero (1987) as suggested by Lee et al. (2000). DIC was measured by standard IR method in the gas phase after acidification of the sample (Goyet and Snover 1993; O'Sullivan and Millero 1998). TA of the sample was calculated based on the potentiometric titration curve (Haraldsson et al.

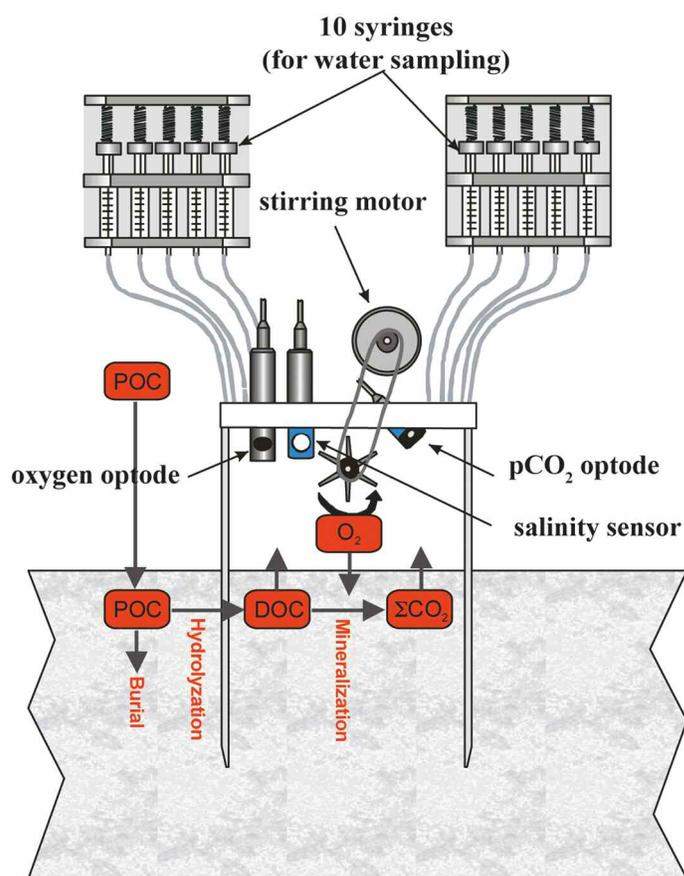


Fig. 4. A schematic view of the Goteborg benthic lander chamber. Changes of concentrations inside the chamber during incubations are registered with sensors for oxygen, pCO₂, and salinity; automated water-sampling system and subsequent analysis allows measurements of other parameters, e.g., nutrients, DIC, CH₄.

Table 1. Performance of pCO₂ sensors in the field.

Sensor	Deployment length/depth	Measured value	Reference value	Error	Accuracy
S/N 28	7 months, 12.6 m	640 μatm	675 μatm	35 μatm	5.18%
S/N 28	6 months, 9.6 m	317 μatm	312 μatm	5 μatm	1.6%
S/N 23	6 months, 5 m	375 μatm	300 μatm	75 μatm	25%
S/N 27	5 months, 12 m	371 μatm	373 μatm	2 μatm	0.54%

1997). High accuracy of the DIC and TA determinations ($\pm 2\text{--}3$ $\mu\text{mol/L}$ for both parameters) was obtained by analyzing Certified Reference Material (CRM) supplied by A. Dickson Laboratory, Scripps Institution of Oceanography.

The software also uses temperature (usually recorded by pCO₂ sensor itself) and salinity (measured using standard conductivity sensors from www.seabird.com and www.aadi.no). Note that CO2SYS software is very sensitive to the set of constants chosen for calculations (for fresh or seawater) and to temperature.

Assessment

Calibration and response time

In this study, sensors were normally calibrated in 40 (or 35) points with respect to eight (or seven) different pCO₂ levels at five different temperatures (Fig. 3). The process of equilibration of the gas mixture with water inside a calibration vessel is relatively slow, especially at low temperatures. This makes a calibration procedure using bubbling of gas mixture rather time-consuming. Therefore, alternative methods of calibration are under investigation.

Fig. 5 shows the response time (τ_{63}) obtained at 0.5°C, 20°C, and 40°C. The responses for the two pCO₂ optodes were similar at the same temperature but quite temperature dependent. The response time was decreasing with increasing temperature as expected. Please note that the range for which the response time was tested was between 5000–50000 μatm , which is a much wider range than the typical 200–1000 μatm found in natural waters. However, the response time is determined by speed of dissolution of CO₂ molecules in the DLR material. These processes are temperature limited, and hence, no significant difference in τ_{63} is expected at lower pCO₂ range.

Calculated values can be summarized as follows:

$$\tau_{63} (0.5^\circ\text{C}) \approx 264 \text{ s}$$

$$\tau_{63} (20^\circ\text{C}) \approx 88 \text{ s}$$

$$\tau_{63} (40^\circ\text{C}) \approx 45 \text{ s}$$

Temperature, preconditioning, bleaching, and pressure effects

Temperature has a significant influence on the behavior of the sensor (see Fig. 3), but since pCO₂ sensors are equipped with in-built temperature sensors, and temperature dependence is included in the calibration procedure, this effect is automatically compensated for by internal processing.

For the first batch of foils that were used in the studies described here, trials demonstrated that before use in marine waters the foils need to be kept wet at all times, using a water-filled protection cap, and preconditioned in salt water. Fig. 6 gives examples of one of the preconditioning investigations that were done and demonstrates that the stabilization, resulting in a change of approximately 12° phase shift, took approximately 1 month. The end result was similar for different sensors, regardless if they were preconditioned in different salinities (17–33), at different temperatures (15°–35°C), or with different LED excitation rate. The significantly different num-

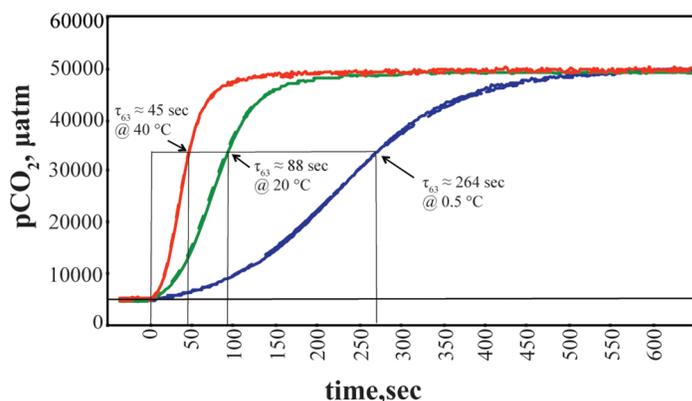


Fig. 5. The response times (τ_{63}) of two pCO₂ sensors: S/N 11 (solid line) and S/N 12 (dashed line) obtained at 0.5 (blue), 20 (green), and 40°C (red).

ber of excitations also indicates that bleaching is not a significant factor if sampling up to the number of excitations used in this case.

The effects of typical estuarine salinity changes on preconditioned and stable sensors are subject to ongoing investigations and will be presented elsewhere.

Pressure tests demonstrated moderate fully reversible influences in the range of -3% for one sensor to -9% for the other at 60 MPa (≈ 6000 dBar ≈ 5900 m water depth). These pressure effects are lower, but appear to be more foil specific and uneven than pressure effects on oxygen optodes carefully studied by Uchida et al. (2008). In this article, pressure effects were found to be about -3.2% per thousand meters water depth corresponding to -19% at 60 MPa for all the tested oxygen optodes.

Poisoning

The measurement principle, that involves pH detection, a priori implies a cross-sensitivity to any acidic or basic gases or vapors. In-house test at PreSens has shown that SO₂, HCl, and acetic acid vapors quickly damage the sensor irreversibly due to their acidic nature.

During a Baltic Sea expedition, four pCO₂ sensors were mounted on the Goteborg benthic lander and logged by a Seaguard instrument (www.aadi.no), which also registered pressure, salinity, oxygen, and temperature information. Two of the pCO₂ sensors were mounted on the lander frame and were measuring ambient pCO₂. Two other pCO₂ optodes were mounted inside the seabed incubation chambers (Fig. 4) and were exposed to sulphidic water as oxygen was depleted inside the chambers during incubations. At times near the recovery of the sensors, the pCO₂ measurement data from inside the chambers were unexpectedly high and the values did not recover when the sensors were placed in H₂S-free water. H₂S in the sensing foil was most probably oxidized to sulphurous acid by oxygen dissolved in the water when the lander was brought to the surface. Strong sulphurous acid had caused contamination of the DLR material inside the foil. Further lab-

oratory experiments confirmed irreversible poisoning of the sensing foils (Fig. 7), which makes these sensors unsuitable for use in environments containing H₂S.

Long-term stability

Several 1-2 month laboratory measurements demonstrated that when foils were properly preconditioned and of good quality, these pCO₂ sensors are stable within 1% of the readings (data not shown).

The longest continuous field deployment lasted for 7 months and was carried out in the Koljo Fjord, on the Swedish west coast, using an on-line cabled observatory providing data in near real-time. A comparison of the pCO₂ time-series from the observatory with reference data, taken on two occasions,

and an inverse correlation with the oxygen measurements demonstrated satisfactory sensor stability (Fig. 8). After 7 months, this sensor was taken up and used for other purposes. Such performance supports the feasibility of 1-year deployments with this type of sensors in coastal dynamic environments like the Koljo Fjord. The environment of the Koljo Fjord at the actual water depth can be broadly described as follows: pCO₂ varied between 300-900 μatm, temperature between 2.5-14.6°C, salinity between 19.4-28, oxygen between 85-440 μM, and currents between 0-30 cm/s.

Other applications

Fig. 9a shows one-month of pCO₂ data from the tank of a land-based salmon hatchery. Variations range from 2-9 mg/L

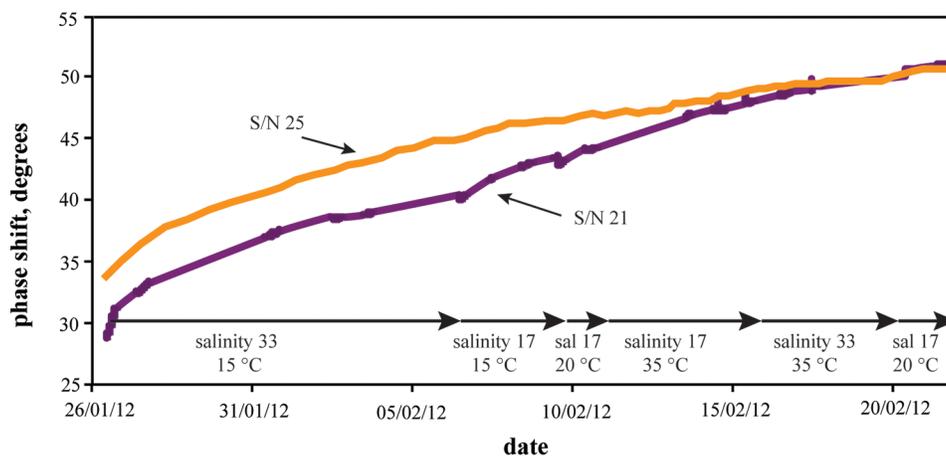


Fig. 6. The results from 1-month preconditioning experiment in the laboratory. Conditions: pCO₂ sensor S/N 25 (orange line)—atmospheric pCO₂ (300-350 μatm), sampling interval 30 s, total number of excitations – 80000, salinity and temperature: see the plot; pCO₂ S/N 21 (cyan line)—sampling interval 30 s (sampling was conducted during 6-8 h per day), total number of excitations – 16000, salinity and temperature: see the plot. End point of preconditioning: pCO₂ sensor S/N 25 – 51.2°, pCO₂ sensor S/N 21 – 51.4° phase shift at atmospheric pCO₂ level.

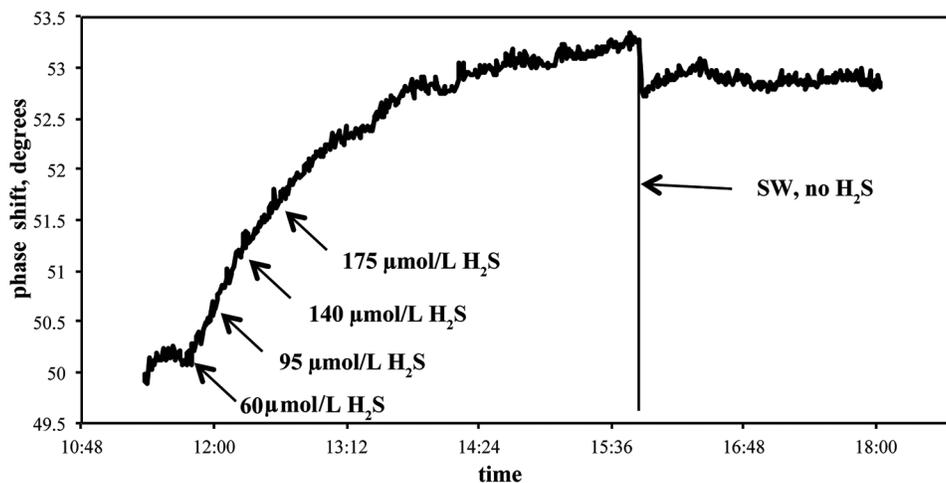


Fig. 7. A laboratory experiment showed irreversible poisoning of pCO₂ sensors by H₂S. The arrows indicate points of addition and resulting concentration of H₂S in a 0.9% NaCl degassed aqueous solution. The line shows the point, when pCO₂ sensor was put into oxygen-saturated seawater (salinity – 33, pCO₂ – 300-350 μatm, room temperature). The difference between the starting value (about 50° phase shift) and end point (52.7°) shows the extent of poisoning with H₂S.

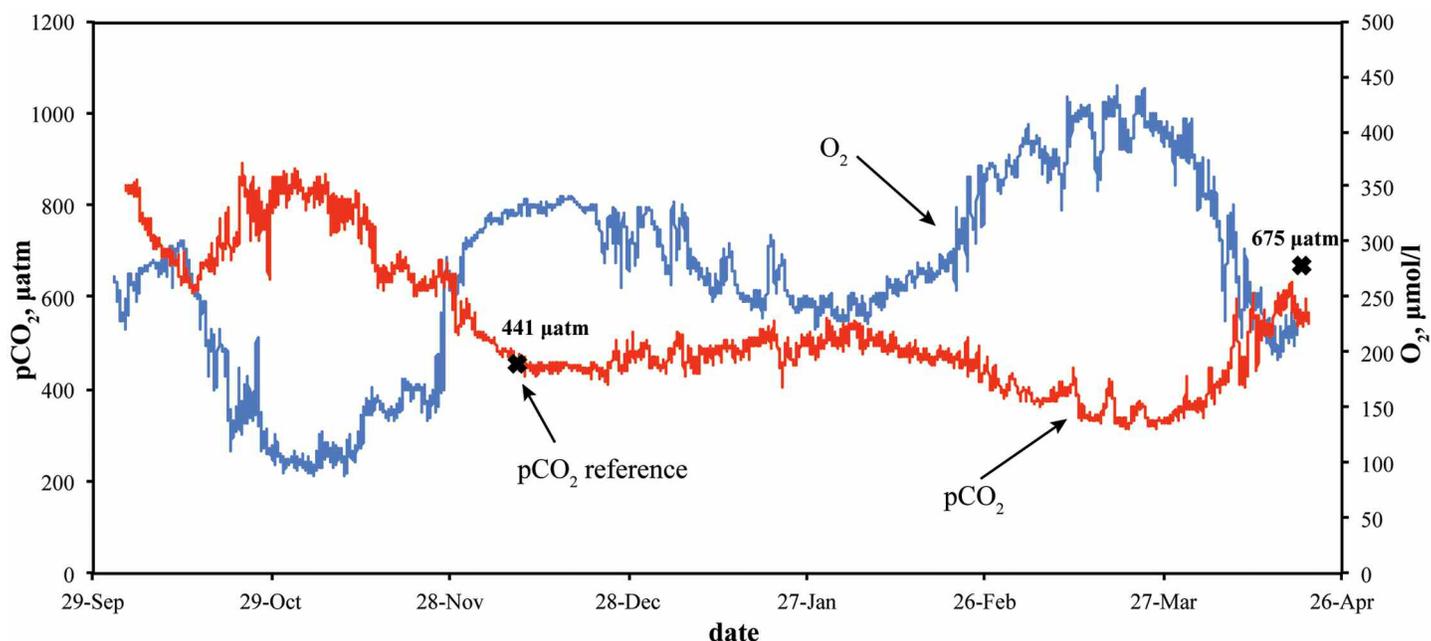


Fig. 8. Performance and long-term stability of the pCO₂ sensor S/N 28 (red) and the O₂ optode (blue) at a water depth of 12.6 m in the Koljo Fjord, Swedish west coast, during a period of 7 months with a sampling interval of 30 min; data are averaged over 2 h. Reference points (x) were calculated from DIC and TA (see “Reference data”). Water samples were taken 8 Dec 2011 and 18 Apr 2012.

(about 500-3000 μatm). Distinct events related to the activity/stress of the fish, e.g., tank cleaning or vaccination could be interpreted from the pCO₂ data. Furthermore, events related to the daily operation of the hatchery could clearly be distinguished (Fig. 9b), including turning on/off lights and feeding.

Fig. 10 shows the uptake of oxygen and the release of CO₂ during one of the benthic chamber incubations using the Goteborg benthic lander. We have made several deployments at different bottoms with different oxygen conditions. With the pCO₂ sensor inside the chamber, it was clearly observed when aerobic oxidation of organic matter terminated and anaerobic respiration took over.

Discussion

A new type of optical pCO₂ sensor was evaluated for a wide range of marine applications. The technology is based on pH change induced by diffusion of CO₂ gas into a pH sensitive DLR material, which is embedded in a hydrophobic matrix in the form of a thin foil. The material is illuminated by an intensity modulated LED and the lifetime of returning luminescent signal, which is pH dependent, is detected and temperature compensated by an internal processor.

These sensors are rated to 6000 m, compact, light, have a wide dynamic range (0-50000 μatm), and consume a fraction of the energy used by other in situ technologies. In laboratory and field work presented in this study multiple sensors were either connected directly to a computer (serial communication) or “plug and play” connected to underwater instruments in larger sensor networks.

The results presented suggest that the tested optode technology is well suited for long-term in situ measurements of pCO₂ in coastal systems. The longest field deployment was 7 months at 30-minute measuring interval, equal to about 10000 measurements, in dynamic conditions (e.g., pCO₂ levels varied from 300-900 μatm). During this period, no sensor drift was detected and valuable information on mixing, air-sea exchange, and primary production/organic matter degradation was collected (unpubl. data).

To work correctly, foils have to be kept humid at all times, and before calibration, they should be preconditioned at similar salinity range as their intended use. For the foils used in this study, preconditioning took about 1 month, and the time needed to reach foil stability appeared to be independent of temperature, number of light excitations, and of salinity variations between 17-33.

Calibration of these sensors is challenging and time consuming. This technology does not have a linear response to changes in pCO₂, which makes multipoint calibrations desirable. The main method used for calibrating the sensors in this study was bubbling water in a temperature-controlled vial with different CO₂/N₂ gas mixtures. In this way, multipoint, normally 40 calibration data points, were obtained. The time for doing a complete calibration run was several weeks. When deploying the sensors in the field, just after calibration, it was still necessary to take water samples for offset adjustments of the readings.

Additional complications when measuring pCO₂ in the field is the complexity of the carbonate system. The offset

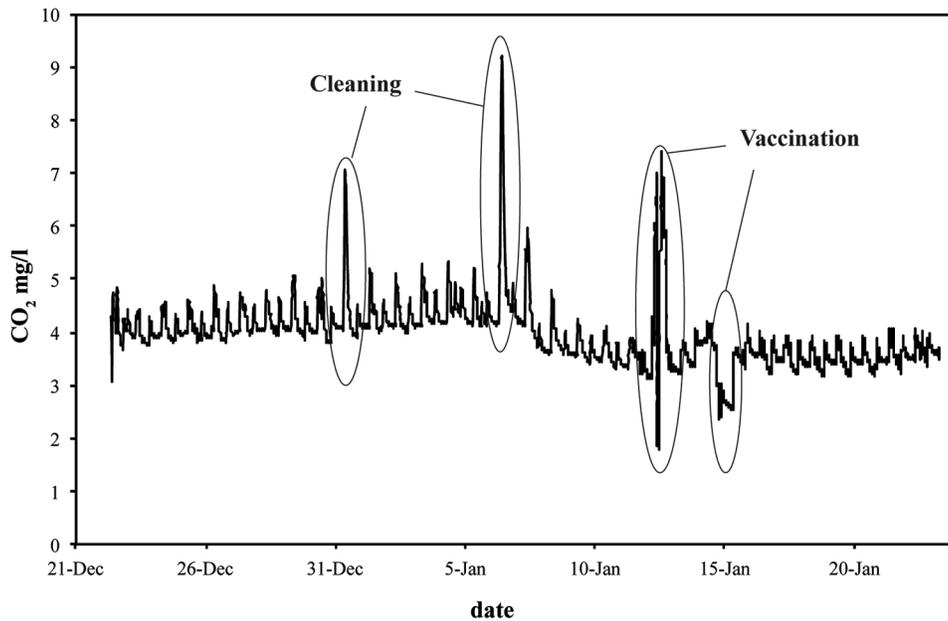


Fig. 9a. Dissolved CO₂ concentration in a fish tank at salmon hatchery. CO₂ was monitored during the period of 1 month with a 1-min interval. Higher amplitude spikes in the plot correspond to additional stress put on the fish (cleaning, vaccination, etc.).

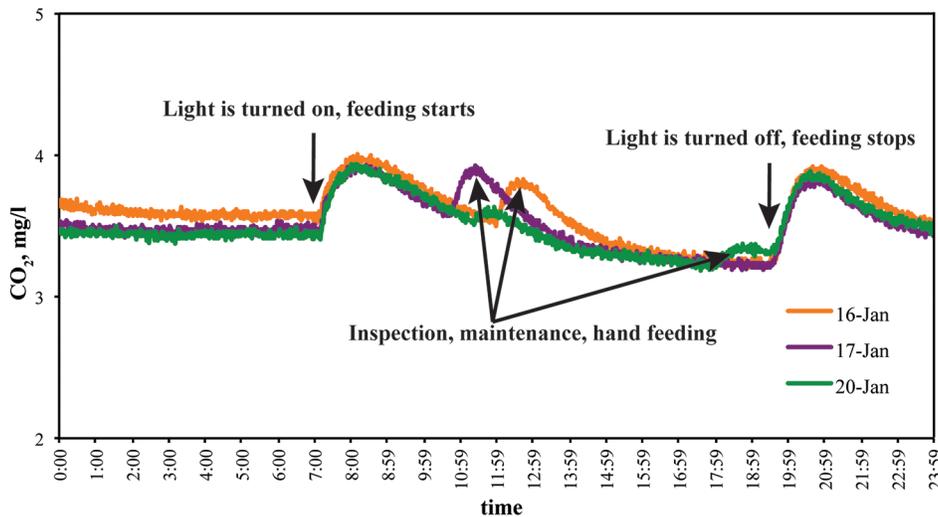


Fig. 9b. Typical dissolved CO₂ daily cycles in a fish tank at salmon hatchery. Three daily cycles are compared (see the legend).

adjustment is based on a calculation of pCO₂ from two other parameters, in this case dissolved inorganic carbon (DIC) and alkalinity (TA), of the carbonate system, and the accuracy of pCO₂ values relies on accurate measurements of these parameters.

In the laboratory, we used the standard deviation of the mean describing 20 consecutive measurements from three different optodes to estimate mean pCO₂ uncertainties (or precision) to be 0.66 % (or 2.7 μatm), 0.45% (or 3.6 μatm), and 0.72% (or 24.45 μatm) for measurements made at around

pCO₂ values of 300 μatm, 800 μatm, and 5000 μatm, respectively. In the field, we believe at best to have obtained absolute accuracies of 0.5% (Table 1). The best precision/resolution that was obtained in the field in this study was approximately ±2 μatm. These data were calculated as an average of 10 consecutive measurements in an open ocean environment with fairly constant conditions (data not shown). Average numbers are significantly worse than specifications given for the best performing infrared or colorimetric instruments, which normally have internal referencing.

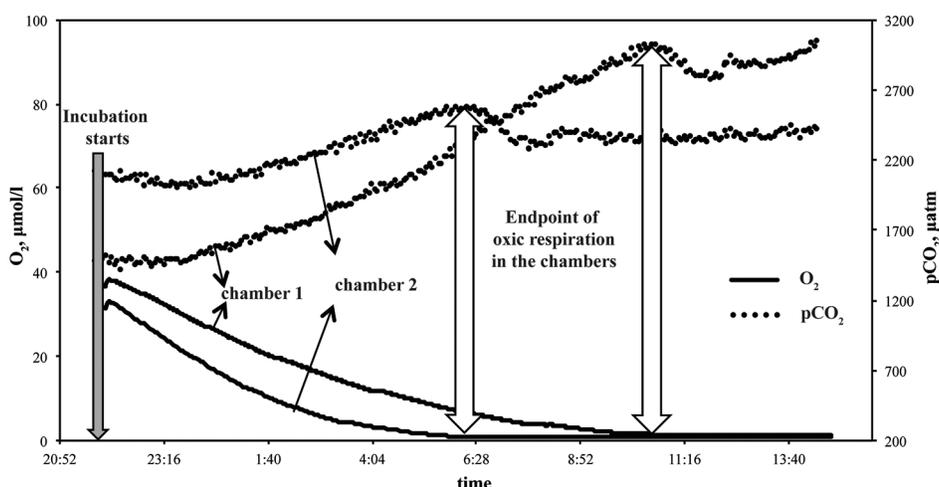


Fig. 10. Oxygen and pCO₂ sensor data during two in situ benthic chamber incubations (station BF25, June 2011, the By Fjord, Swedish west coast). Consumption of oxygen (solid line) is followed by release of CO₂ (dotted line) from the sediment during aerobic respiration processes; when oxygen is depleted, the release of CO₂ stops (indicated with white arrows). Anaerobic respiration leads to the production of carbonate system species other than CO₂.

The response time, about 5 min in cold water, is limited by CO₂ diffusion into the foil and is similar to other technologies. This response time makes it difficult to use these sensors on profiling/moving platforms.

The sensors gave 3-9% lower readings at 600 bar (equals about 5900 m water depth), which is lower pressure dependence than demonstrated for oxygen optodes (Uchida et al. 2008), which showed 19% lower readings at 600 bar. No pressure hysteresis could be detected; when pressure was released, the sensors immediately returned to the same readings as before pressure was applied.

A limitation of this technology is that it should not be used in sulphidic environments, because it is cross sensitive to hydrogen sulphide (H₂S). When the foil is exposed to H₂S and then is brought into normal (oxic) conditions, it becomes irreversibly poisoned, probably due to formation of sulphurous acid inside the foil. The poisoning continues to increase the response signal as long as the sensor is exposed to H₂S.

To conclude, these sensors have a wide dynamic range, and size and energy consumption advantages, compared with existing in situ technologies, which make them well suited for multisensor array studies with variable and/or high concentrations, e.g., in coastal studies and in aquaculture. The long-term stability and precision should also be adequate for many other applications. To use these sensors to study dynamics of the open ocean carbonate system, the absolute accuracy needs to be improved.

Comments and recommendations

Future work to improve this technology could include ameliorations of the foil so that response times are shorter, and different foils get more similar responses. Of relevance should be multivariate tests to assess to what extent factors other than those studied here have an influence on the sensor response

and whether the factors already studied interact with each other (e.g., Bertsson et al. 1997; Tengberg et al. 2006). Further studies of pressure effects on the sensor and investigations of the salinity effects should be highly relevant and of interest. There should also be room for significant improvements/simplification of the calibration methods. More and longer field tests at faster sampling are ongoing and needed to reveal any additional limitations of this technology. Also the effect of biofouling, essential to assure data quality in many aquatic studies, should be studied more thoroughly.

References

- Almroth, E., A. Tengberg, H. Andersson, S. Pakhomova, and P. O. J. Hall. 2009. Effects of resuspension on benthic fluxes of oxygen, nutrients, dissolved inorganic carbon, iron and manganese in the Gulf of Finland, Baltic Sea. *Cont. Shelf Res.* 29:807-818 [doi:10.1016/j.csr.2008.12.011].
- Almroth-Rosell, E., A. Tengberg, S. Andersson, A. Apler, and P. O. J. Hall. 2012. Effects of simulated natural and massive resuspension on benthic oxygen, nutrient and dissolved inorganic carbon fluxes in Loch Creran, Scotland. *J. Sea Res.* 72:38-48 [doi:10.1016/j.seares.2012.04.012].
- Bertsson, M., A. Tengberg, P. O. J. Hall, and M. Josefsson. 1997. Multivariate experimental methodology applied to the calibration of a Clark type oxygen sensor. *Anal. Chim. Acta* 355:43-53 [doi:10.1016/S0003-2670(97)81610-8].
- Bozec, Y., and others. 2011. Diurnal to inter-annual dynamics of pCO₂ recorded by a CARIOCA sensor in a temperate coastal ecosystem (2003-2009). *Mar. Chem.* 126:13-26 [doi:10.1016/j.marchem.2011.03.003].
- Culbertson, C. H., and R. M. Pytkowicz. 1968. Effect of pressure on carbonic acid, boric acid, and the pH of seawater. *Limnol. Oceanogr.* 13:403-417 [doi:10.4319/lo.1968.13.3.0403].

- DeGrandpre, M. D. 1993. Measurement of seawater pCO₂ using a renewable-reagent fiber optic sensor with colorimetric detection. *Anal. Chem.* 65:331-337 [doi:10.1021/ac00052a005].
- , T. R. Hammar, S. P. Smith, and F. L. Sayles. 1995. In situ measurements of seawater CO₂. *Limnol. Oceanogr.* 40:969-975 [doi:10.4319/lo.1995.40.5.0969].
- Dickson, A. G. and F. J. Millero. 1987. A comparison of the equilibrium constants for the dissociation of carbonic-acid in seawater media. *Deep-Sea Res. Part A.* 34:1733-1743 [doi:10.1016/0198-0149(87)90021-5].
- Emerson, S. R., and J. L. Hedges. 2008. *Chemical oceanography and the marine carbon cycle*. Cambridge Univ. Press [doi:10.1017/CBO9780511793202].
- Goyet, C., D. R. Walt, and P. G. Brewer. 1992. Development of a fiber optic sensor for measurement of pCO₂ in seawater: design criteria and sea trials. *Deep-Sea Res. A* 39:1015-1026 [doi:10.1016/0198-0149(92)90037-T].
- , and A.K. Snover. 1993. High-accuracy measurements of total dissolved inorganic carbon in the ocean: comparison of alternate detection methods. *Mar. Chem.* 44:235-242 [doi:10.1016/0304-4203(93)90205-3].
- Haraldsson, C., L. G. Anderson, M. Hasselov, S. Hulth, and K. Olsson. 1997. Rapid, high-precision potentiometric titration of alkalinity in ocean and sediment pore waters. *Deep-Sea Res.* 44:2031-2044 [doi:10.1016/S0967-0637(97)00088-5].
- Kaltin, S., and L. G. Anderson. 2005. Uptake of atmospheric carbon dioxide in Arctic shelf seas: evaluation of the relative importance of processes that influence pCO₂ in water transported over the Bering–Chukchi Sea shelf. *Mar. Chem.* 94:67-79 [doi:10.1016/j.marchem.2004.07.010].
- Klimant, I., C. Huber, G. Liebsch, G. Neurauder, A. Stangelmayer, and O. S. Wolfbeis. 2001. Dual lifetime referencing (DLR): a new scheme for converting fluorescence intensity into a frequency-domain or time-domain information, p 257-274. *In* B. Valeur and J.C. Brochon [eds.], *New trends in fluorescence spectroscopy: Application to chemical and life sciences*. Springer Verlag.
- Lee, K., F. J. Millero, R. H. Byrne, R. A. Feely, and R. Wanninkhof. 2000. The recommended dissociation constants for carbonic acid in seawater. *Geophys. Res. Lett.* 27(2):229-232 [doi:10.1029/1999GL002345].
- Lefèvre, N., J. P. Ciabrini, G. Michard, B. Briant, M. DuChaufaut, and L. Merlivat. 1993. A new optical sensor for pCO₂ measurements in seawater. *Mar. Chem.* 42:189-198 [doi:10.1016/0304-4203(93)90011-C].
- Lewis, E., and D. Wallace. 1998. Program developed for CO₂ system calculations. Carbon dioxide information analysis center. Oak Ridge National Laboratory [doi:10.2172/639712].
- Liebsch, G., I. Klimant, C. Krause, and O. S. Wolfbeis. 2001. Fluorescent imaging of pH with optical sensors using time domain dual lifetime referencing. *Anal. Chem.* 73:4354-4363 [doi:10.1021/ac0100852].
- Mehrbach, C., C. H. Culbertson, J. E. Hawley and R. M. Pytkowicz. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18:897-907 <http://aslo.org/lo/toc/vol_18/issue_6/0897.pdf>.
- O'Sullivan, D. W., and F. J. Millero. 1998. Continual measurement of the total inorganic carbon in surface seawater. *Mar. Chem.* 60:75-83 [doi:10.1016/S0304-4203(97)00079-0].
- Sarmiento, J. L., and N. Gruber. 2006. *Ocean biogeochemical dynamics*, Princeton, Woodstock. Princeton University Press.
- Takahashi, T., and others. 2009. Climatological mean and decadal changes in surface ocean pCO₂, and net sea-air CO₂ flux over the global oceans. *Deep-Sea Res II* 56:554-577 [doi:10.1016/j.dsr2.2008.12.009].
- Tamburri, M. N., and others. 2011. Alliance for coastal technologies: Advancing moored pCO₂ instruments in coastal waters. *Mar. Technol. Soc. J.* 45:43-51 [doi:10.4031/MTSJ.45.1.4].
- Tengberg, A., and others. 2006. Evaluation of a lifetime based optode to measure oxygen in aquatic systems. *Limnol. Oceanogr. Methods* 4:7-17 [doi:10.4319/lom.2006.4.7].
- Thomas, H., and B. Schneider. 1999. The seasonal cycle of carbon dioxide in Baltic Sea surface waters. *J. Mar. Syst.* 22:53-67 [doi:10.1016/S0924-7963(99)00030-5].
- , Y. Bozec, K. Elkalay, and H. J. W. de Baar. 2004. enhanced open ocean storage of CO₂ from shelf sea pumping. *Science* 304:1005-1008 [doi:10.1126/science.1095491].
- Uchida, H., T. Kawano, I. Kaneko, and M. Fukasawa. 2008. In situ calibration of optode-based oxygen sensors. *J. Atmos. Ocean. Tech.* 25:2271-2281 [doi:10.1175/2008JTECH0549.1].
- Viktorsson, L., and others. 2012. Benthic phosphorus dynamics in the Gulf of Finland, Baltic Sea. *Aquat. Geochem.* 18:543-564 [doi:10.1007/s10498-011-9155-y].
- , N. Ekeröth, M. Nilsson, M. Kononets, and P. O. J. Hall. 2013. Phosphorus recycling in sediments of the central Baltic Sea. *Biogeosciences* 10:3901-3916 [doi:10.5194/bg-10-3901-2013].
- von Bültzingslöwen, C., A. K. McEvoy, C. McDonagh, B. D. MacCraith, I. Klimant, C. Krause, and O. S. Wolfbeis. 2002. Sol-gel based optical carbon dioxide sensor employing dual luminophore referencing for application in food packaging technology. *Analyst* 127:1478-1483 [doi:10.1039/b207438a].
- Wayne, R. P. 2000. *Chemistry of atmospheres*, 3rd ed. Oxford Univ. Press.
- Weiss, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Mar. Chem.* 2:203-215 [doi:10.1016/0304-4203(74)90015-2].
- Wesslander, K., and others. 2011. Observed carbon dioxide and oxygen dynamics in a Baltic Sea coastal region. *J. Mar.Syst.* 86:1-9 [doi:10.1016/j.jmarsys.2011.01.001].

Submitted 25 December 2012

Revised 24 November 2013

Accepted 23 January 2014