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Development and use of an optical pCO$_2$ sensor in marine studies

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Abstract

Partial pressure of CO_2 (pCO_2) is one of the most important parameters, which are measured in the global ocean in conjunction with ocean acidification studies. It is also a parameter of great interest to aquaculture and fish industries since CO_2 in large amounts is highly toxic for animals. The requirements for pCO_2 measuring systems, e.g. long-term stability, accuracy, high sampling frequency, easy maintenance, low-power consumption, are based on the demands from the industry and scientific community, and the current trends according to global sensor development initiatives.

A newly developed fluorescence lifetime based optical sensor for measuring pCO_2 in water was evaluated and described (Paper 1). The advantages and drawbacks of this new technology in comparison to existing methods were discussed and compared in a number of *in situ* field deployments (Papers 1-3). A cross-sensitivity of the pCO_2 optode to the most commonly co-existing substances in water and seawater was evaluated (Papers 1 and 3). A number of parameters, which influence the response of the pCO_2 sensor, were thoroughly investigated in a specially designed experiment and assessed using a multivariate data analysis approach (Paper 1, 4). We have especially focused on describing the influence of salinity change and hydrostatic pressure on the sensor response in separate laboratory tests (Paper 4). A simplified calibration procedure for narrow ranges of pCO_2 was proposed and a practically usable mathematical calibration model was elaborated and verified (Paper 4). As a result of sensor development efforts in achieving stability and accuracy of the sensor, pre-conditioning and single-point referencing procedures were proposed (Paper 1).

The developed pCO_2 sensor was successfully used in a number of biogeochemical studies (Paper 2), for monitoring pCO_2 levels in fish tanks (Paper 1) and for detecting CO_2 leakages out of a simulated sub-seabed Carbon Capture Storage site (CCS) (Paper 3). Long-term high-temporarily resolved pCO_2 data in combination with other sensor data (especially oxygen), gave us a deep insight into the governing processes (such as air-sea exchange, vertical mixing, primary production, organic mater degradation), which drive seasonal changes in the carbonate system of the Koljo Fjord, western Sweden. In the same study, stability of the sensor over a year of continuous measurements was confirmed. Due to its excellent performance, the pCO_2 sensor has found its well-deserved place as a part of warning/monitoring systems in the proposed strategy for detection of CO_2 leakage out of CCS sites.

The range of potential applications for the pCO_2 sensor is obviously wide. This challenge stimulates further development and improvements of the sensor, especially in accuracy and tolerance to salinity changes. These tasks are being addressed and investigations are in progress.

Keywords: pCO_2 | O_2 | sensor | optode | cross-sensitivity | carbonate system of seawater | biogeochemistry | Redfield ratio | the Koljo Fjord | cabled observatory | CCS | QICS | environmental engineering | leakage detection | MVDA | DoE

Populärvetenskaplig sammanfattning

Koldioxid (CO_2) är en av de gaser, som vanligtvis mäts i havet i samband med studier av den globala uppvärmningen och havets försurning. Den globala oceanen speglar förändringar av CO_2 i atmosfären, vilket leder till försurning av havsvatten, som hotar välbefinnandet av havets organismer. Koldioxid är också av stort intresse för vattenbruk och fiskindustrier eftersom CO_2 i stora mängder kan orsaka kvävning av den odlade fisken.

Det är inte en lätt uppgift att mäta CO_2, eftersom oorganiskt kol kan finns i många former, och en form lätt kan omvandlas till en annan. Men under det senaste århundradet har forskare kunnat förklara hur dessa förändringar sker och kunnat beskriva dem. Partialtrycket av CO_2-gas (pCO_2) är en av de parametrar som beskriver mängden löst oorganiskt kol i vatten.

Utveckling av nya instrument för att mäta pCO_2 har sina utmaningar. CO_2-gas måste extraheras från vattnet innan mätningarna, och instrument ska kunna mäta mycket små mängder CO_2; från ca 0.01 mol % till 1 mol %. Men det finns också ett behov av att mäta CO_2 kontinuerligt under långa tidsperioder för att beskriva förändringar i det globala havet från år till år som en följd av klimatförändringar, och för att observera när CO_2-nivåerna i t.ex. tankar för fiskodling blir farligt höga. Det senare fallet är också ett exempel på en situation då varningssystem för farliga CO_2-nivåer behöver utvecklas.

En nyutvecklad sensor för mätning av pCO_2 i vatten beskrivs i denna doktorsavhandling. Den är liten, kompakt, stabil, fungerar autonomt, och kan mäta så låga koncentrationer som 0.01 mol % CO_2. Vi har visat att sensorn fungerar i havet under mer än sju månader utan avbrott. Vi har utfört mycket arbete för att förbättra sensorn så att den kan leverera tillförlitliga mätningar av pCO_2.

Vi använde pCO_2 sensorn i våra vetenskapliga studier av Koljöfjorden, västra Sverige. Studierna omfattade bl.a. att upptäcka när vårblomningen börjar, hur länge den varar, och hur den påverkar koncentrationerna av löst oorganiskt kol och syrgas, samt förhållandet mellan dessa ämnen. En annan viktig tillämpning av sensorn var att upptäcka läckage av CO_2 till havsvatten från platser där lagring av CO_2 (s.k. *Carbon Capture Storage (CCS)*) sker. Det har nyligen föreslagits att överskott av CO_2, som produceras genom t.ex. förbränning av fossila bränslen, kan pumpas ned i hålrum under havsbottnen, varifrån gas eller olja tidigare utvunnits. Riskerna med sådana installationer är läckage av CO_2 till följd av brott av rör, som levererar gasen, eller sprickor i berg under havsbotten. Detta skulle skapa högre pCO_2 i vattnet, vilket sensorn kan detektera, och därmed kan läckaget upptäckas och åtgärder vidtas.

Vi fortsätter att arbeta på att ytterligare förbättra sensorn, så att den t.ex. kan mäta mycket små förändringar av pCO_2, och testa den under olika förhållanden i fält. Vi hoppas att sensorn kommer att bli ett användbart verktyg för forskare, såsom den varit för oss, och att den kommer att bidra till att besvara många aktuella forskningsfrågor.

Part A: Table of Contents

Part B: List of publications

   I.   **Performance of a lifetime-based optode for measuring partial pressure of carbon dioxide in natural waters.**
Atamanchuk D, Tengberg A, Thomas PJ, Hovdenes J, Apostolidis A, Huber C, Hall POJ.
Limnol Oceanogr Methods (conditionally accepted for publication)

  II.   **Continuous long-term observations of the carbonate system dynamics in the water column of a temperate fjord.**
Atamanchuk D, Kononets M, Thomas PJ, Hovdenes J, Tengberg A, Hall POJ.
Marine Chemistry (submitted)

 III.   **Field-testing of methods and strategies to detect CO_2 leakage from a simulated sub-seabed storage site**
Atamanchuk D, Tengberg A, Aleynik D, Hall POJ, Stahl H.
Manuscript

  IV.   **Multivariate evaluation of an optical pCO_2 sensor for oceanographic measurements**
Atamanchuk D, Tengberg A, Thomas PJ, Hovdenes J, Berntsson M, Hall POJ.
Manuscript

Abbreviations

pCO_2	partial pressure of CO_2 gas
fCO_2	fugacity of CO_2 gas
TCO_2, DIC, TC, TIC, C_T	total dissolved inorganic carbon
DLR	Dual Lifetime Referencing
TA, A_T	total alkalinity
CA	carbonate alkalinity
A_{Tsal}	salinity-derived alkalinity
HOT/ALOHA	Hawaii Ocean Time-series/A Long-Term Oligotrophic Habitat Assessment
BATS	Bermuda Atlantic Time-series Study
ESTOC	European Station for Time series in the OCean
AZMP	the Atlantic Zone Monitoring Program
CCS	Carbon Capture and Storage
QICS	Quantifying and monitoring potential ecosystem Impacts of geological Carbon Storage
ISFET	Ion-Sensitive Field-Effect Transistor
MVDA	MultiVariate Data Analysis

1. Introduction

Carbon dioxide (CO_2) is crucial in the functioning of the global ocean, the atmosphere and living organisms. Only a very small fraction (in the order of ppm) of the oceanic dissolved inorganic carbon pool exists as CO_2 gas. CO_2 is an intermediate compound in most of the changes related to carbon in the hydrosphere, atmosphere and in exchanges between these two spheres. Carbon in the form of CO_2 gas takes part in biological processes, and in the same gaseous form it is absorbed from the atmosphere to the ocean, where it is eventually converted to the dissolved carbonate system. Significant work has been done to establish the pathways of CO_2 transformation and circulation in the global ocean, and the kinetics and dynamics of the processes. In that perspective, CO_2 measurements are highly relevant and essential in assessing the role of the ocean in global carbon cycling.

This work is dealing with the development and use of an optical sensor (optode) for measuring partial pressure of CO_2 gas (pCO_2) in aquatic environments. The operational and measurement principle of the pCO_2 optode was described. Stability, accuracy and precision of the sensor were evaluated in a number of laboratory and field tests. The pCO_2 optodes were successfully applied in several scientific studies as part of the observing systems (the Koljo Fjord Observatory, the QICS monitoring system), and as stand-alone alternatives, where they showed a satisfactory performance. Interfering factors in pCO_2 measurements while using the optode (poisoning of hydrogen sulfide, osmotic effect on the foil) were documented as well as a response of the sensor to various changes in the water parameters (temperature, salinity, pressure).

2. The carbonate system of seawater

2.1. pCO₂ and the carbonate system of seawater

Dissolved carbon dioxide (CO_2) in the ocean occurs mainly in three inorganic forms: free aqueous carbon dioxide ($CO_2(aq)$), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). A minor form is true carbonic acid (H_2CO_3), whose concentration is less than 0.3% of $[CO_2(aq)]$. The sum of $[CO_2(aq)]$ and $[H_2CO_3]$ is denoted as $[CO_2]$. In thermodynamic equilibrium, gaseous carbon dioxide $[CO_2(g)]$ and $[CO_2]$ are related by Henry's law:

$$CO_2(g) \overset{K_0}{=} [CO_2]$$

where K_0 is the temperature- and salinity-dependent solubility coefficient of CO_2 in seawater (Weiss, 1974). The concentration of dissolved CO_2 and the fugacity of gaseous CO_2, $f$$CO_2$, then obey the equation

$$[CO_2] = K_0 \times fCO_2,$$

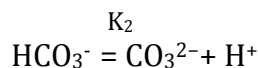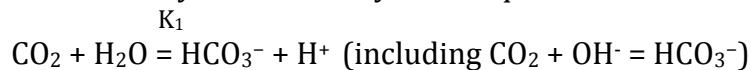where the fugacity is virtually equal to the partial pressure, pCO_2.

Fugacity is an expression for the concentration of a *real* gas in a mixture of real gases, whereas partial pressure is an expression for the concentration of an *ideal* gas in a mixture of ideal gases. Ideal gases are conceptualized as comprising molecules which occupy no volume and between which no forces exist. The concept of fugacity is introduced in order to use for real gases the thermodynamic relationships established for ideal gases. Fugacity cannot be measured directly, as pressure can.

The thermodynamic equation of state for ideal gases is

$PV=nRT$,

where P is pressure, V is volume, n is number of moles of gas, R is the gas constant, and T is absolute temperature. This equation can be used to convert the number of moles of pure, ideal gas to the pressure of the gas. CO_2 is a highly non-ideal gas, especially at low pressures. The negative deviation from ideality at low pressures suggests attractive forces between CO_2 molecules. The significance of this factor becomes less important at higher pressures. The approximation of ideality for CO_2 may be acceptable at ambient pressures when high accuracy is not required. The difference between pressure and fugacity for a typical ambient CO_2 concentration is 1 to 1.5 µatm (~0.3%) over the temperature range 0 to 30°C.

The dissolved carbonate species react with water, hydrogen ions, and hydroxyl ions and they are related by these equilibria:

$$CO_2 + H_2O \overset{K_1}{=} HCO_3^- + H^+ \text{ (including } CO_2 + OH^- = HCO_3^-)$$

$$HCO_3^- \overset{K_2}{=} CO_3^{2-} + H^+$$

The pK = −log(K) of the stoichiometric dissociation constants of carbonic acid in seawater are pK_1 = 5.94 and pK_2 2= 9.13 at temperature = 15°C , salinity S = 35, and surface pressure P = 1 atm (Prieto & Millero 2001). At a typical surface-seawater pH of 8.2, the speciation between $[CO_2]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ is 0.5%, 89% and 10.5%, respectively, showing that most of the dissolved carbonate system exists in the form of HCO_3^- and not in the form of CO_2. The sum of the dissolved carbonate species is denoted total dissolved inorganic carbon (TCO_2):
$TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$

This quantity is also referred to as DIC, C_T, TIC or TC, where all symbols mean total dissolved inorganic carbon.

Another essential parameter to describe the carbonate system in seawater is the total alkalinity (TA or A_T), which is a measure of the charge balance in seawater. The carbonate alkalinity (CA) is a part of TA, and is often used instead of TA for simplification in the calculations (when borate concentration is unknown).

TA = CA + [OH$^-$] + [B(OH)$_4$$^-$] – [H$^+$] + minor contributors

CA = [HCO$_3$$^-$] + 2[CO$_3$$^{2-}$]

DIC, TA, pCO$_2$ and pH are linked through the mentioned equations, which allow the calculations of carbonate system variables knowing any two of these four (details are in Zeebe and Wolf-Gladrow 2001, and references therein).

2.2. Calculations of the carbonate system of seawater

Figure 1 gives information about the composition of the carbonate system depending on the pH. From this figure it is described how the carbonate system species are related through a set of dissociation constants. The influence of salinity, temperature and pressure on the dissociation constants was described and discussed in Culberson and Pytkowicz (1968), Hansson (1973), Mehrbach et al. (1973), Goyet and Poisson (1989), Roy et al. (1993), Mojica-Prieto and Millero (2002). Thus knowing these parameters, it is possible to perform calculations of the carbonate system.
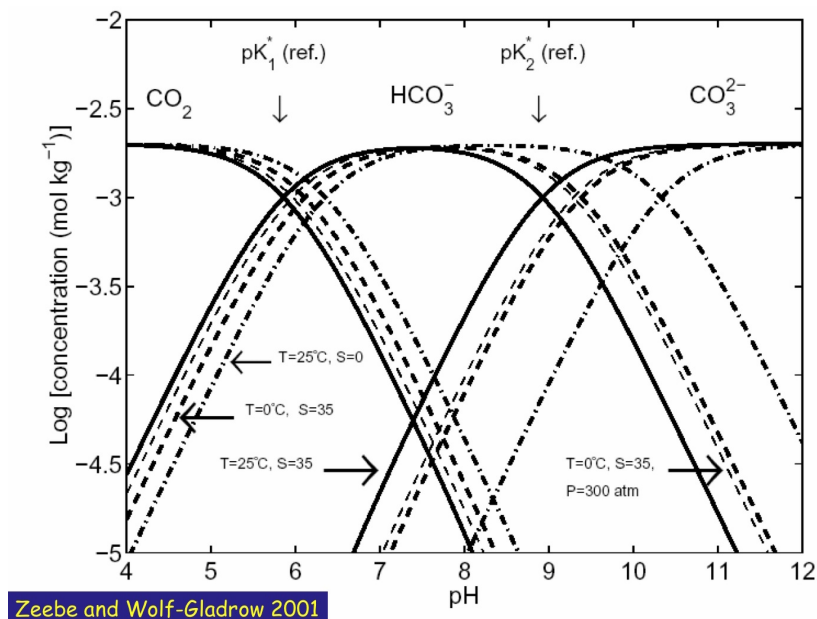

Fig. 1. Speciation of TCO$_2$ in seawater vs pH depending on temperature and salinity. Figure is taken from Zeebe and Wolf-Gladrow (2001).

In our calculations of the carbonate system, we used the CO2SYS software (Lewis and Wallace (1998), http://cdiac.ornl.gov/oceans/co2rprt.html), which comprehends all known equations related to the carbonate system.

When performing calculations, one should be aware of possible errors due to uncertainties in input parameters (Table 1).

Parameter	Calculation method	pH	A_T (μeq kg^{-1})	DIC (μmol kg^{-1})	f_{CO_2} (μatm)
Measurement error		0.0020	4.0	2.0	2.0
Calculated error (methods I and II)					
pH-A_T	I			3.8	2.1
	II			2.4	1.7
pH - DIC	I		2.7		1.8
	II		2.6		1.6
pH $- f_{CO_2}^w$	I		21	21	
	II				
$f_{CO_2}^w$ - DIC	I	0.0025	3.4		
	II	0.0019	2.6		
$f_{CO_2}^w$ - A_T	I	0.0026		3.2	
	II	0.0019		2.1	
A_T - DIC	I	0.0062			5.7
	II	0.0036			2.9

Table 1. Estimates of the errors in measurement and calculation of the carbonate system parameters (data from Millero, 1995). All values are standard deviations about the mean. Measurement error is based on comparison to standard values. Calculated error is determined either by: (I) compounding errors in the analytical accuracy of the input values assuming equilibrium constants are perfect; or (II) compounding errors in the first and second dissociation constants assuming the measurements are perfect. The total error of the calculated estimate would involve compounding these two errors. Table is taken from Emerson and Hedges (2008).

Data from Table 1 should also be taken into account when choosing two parameters for calculations of the carbonate system. For example, the combination of pCO_2 and pH measurements will give the biggest error in TA and DIC estimations, and thus this combination of input parameters should be avoided. On the other hand, the errors predict possible discrepancies between the measured values and calculated ones. This is important to know, when the accuracy of the sensors is verified versus the results from calculations.

A set of chosen constants can also influence the accuracy of calculations. Discussions around the appropriate constants for the calculations have been a hot topic over the last decades. The recommendations on which option to choose depend on multiple factors and are given in Lee et al. (1996, 2000) and Lueker et al. (2000).

2.3. The utility of relations within the carbonate system for biogeochemical studies

The ocean carbon cycle is complex and is a combination of a number of biogeochemical forcings (Fig. 2), each of which steer one or several carbonate system components (parameters).
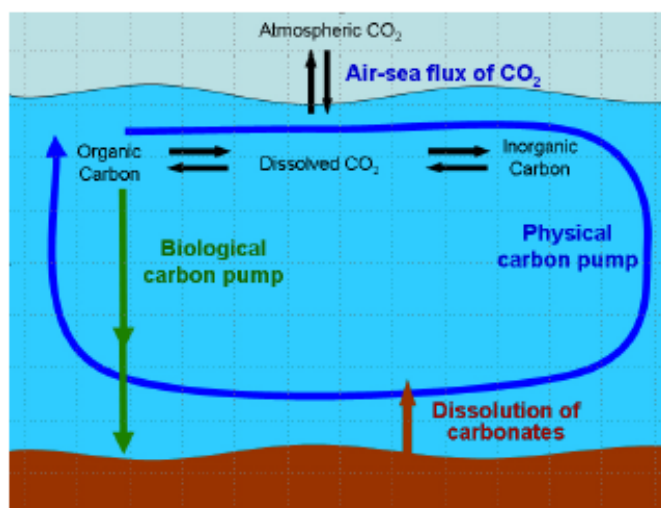

Fig. 2. Schematic view of the oceanic carbon cycle, including air-sea flux, biological pump, physical pump and dissolution of carbonates. Figure is taken from Schuster et al. (2009).

It is usually impossible to have a satisfactory spatio-temporal coverage of all four parameters of the carbonate system of seawater. However, these kinds of observations are the most effective in addressing the role of air-sea exchange, biological pump, and acidification in the functioning of the global ocean as well as for C-budget modelling. Direct autonomous *in situ* measurement techniques for DIC and A$_T$, that will satisfy the demands, do not exist to the best of our knowledge, and measurements of pCO$_2$ and/or pH are thus the most commonly used. Continuous pCO$_2$ time-series using submersible instruments were successfully recorded previously (DeGrandpre et al., 1995) and used for the estimation of air-sea CO$_2$ fluxes and biologically induced *in situ* changes (Friedrich et al., 1995; Hood et. al., 1999; Alvares et al., 2002; Gago et al., 2003; Carillo et al., 2004; Kuss et al., 2006; Körtzinger et al., 2008a, b). Cullison Gray et al. (2011) have shown a successful application of an *in situ* pH time-series in calculations of the marine inorganic carbon system.

In practice, pCO$_2$ or pH time-series and indirect measurements of A$_T$ (estimated from salinity or temperature) are usually used for calculation of the other parameters of the carbonate system. Körtzinger et al. (2008a,b) used observed pCO$_2$ and salinity derived measurements of climatological total alkalinity in the calculation of DIC.

We have used a similar approach to describing the biogeochemical processes, which dominate during different seasons in the Koljo Fjord (Paper 2). We have established alkalinity-salinity relationship (A$_{Tsal}$) in the Koljo Fjord in order to

use continuously recorded salinity data as a proxy for alkalinity. DIC values were then calculated from measured pCO_2 and A_{Tsal}. An example of such data is given in Fig. 3.
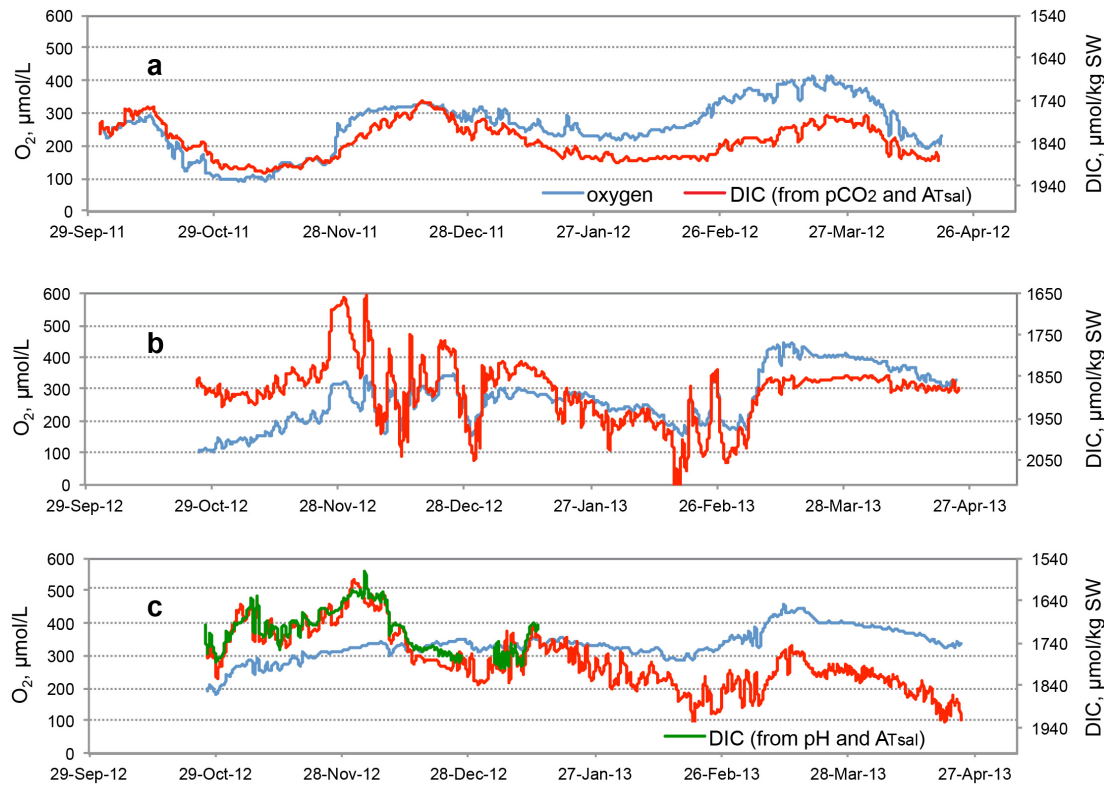

Fig. 3. Relationships between calculated low-pass filtered (>24 hours period) DIC and measured oxygen time-series at (a) 12.6 m (2011-2012), (b) 9.6 m (2012-2013) and (c) 5 m (2012-2013) in the Koljo Fjord. Note: DIC values are presented on a reverse scale. The axes of each filtered concentrations are scaled to span the similar range when normalized to the Redfield ratio (DIC:O_2 = 106:138). Panel c shows an agreement between DIC values calculated from A_{Tsal} and pH (green), and A_{Tsal} and pCO_2 (red). (Figure is taken from Paper 2).

High-quality pCO_2 data from the newly-developed sensor, complimented by data from ca. 50 different other sensors measuring e.g. oxygen, salinity, temperature, chlorophyll A, pH/ORP, and currents, were recorded at different water depths with 30 min interval during a period of two years in the Koljo Fjord. These long-term observations allowed us to specify:
- various physical and biogeochemical processes influencing the carbonate and oxygen systems of the fjord;
- dominance of different processes during different parts of the seasonal cycle in influencing inorganic carbon and oxygen inventories;
- stoichiometry of primary production in the fjord, which then was compared to classical Redfield O:C ratios.

This type of high-temporal data collection thus opens new possibilities in understanding and characterizing processes taking place in a marine basin.
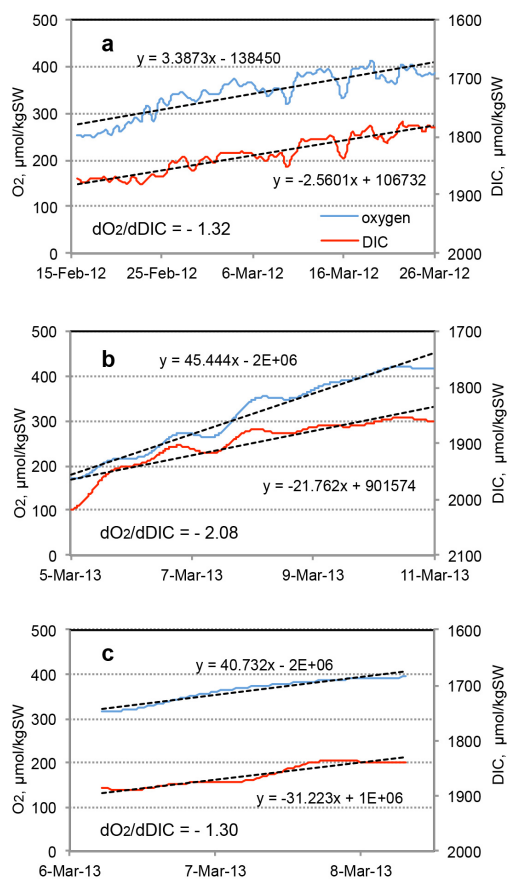
Fig. 4. Calculation of net primary production rates in the Koljo Fjord at depths of (a) 12.6 m (2011-2012), (b) 9.6 m (2012-2013), and (c) 5 m (2012-2013). The slopes of corresponding linear trend lines are used to calculate the ratio of the absolute change in concentrations (ΔO$_2$/ΔDIC) indicated in the plots. Note: DIC values are presented on a reverse scale. (Figure is taken from Paper 2).

The production and consumption of O$_2$ and CO$_2$ during build-up and remineralization of organic matter (OM) in the ocean occur at rather well-constrained O$_2$:C ratios. Körtzinger et al. (2001) found a value of -1.34±0.06 (ΔO$_2$/ΔDIC) for remineralization in the main thermocline. It was also shown that the original value of -1.30 by Redfield et al. (1963) and the value -1.45±0.015 of Anderson and Sarmiento (1994) were at the upper and the lower end of the biochemically plausible range. Because of the concomitant large impact of biological fluxes, air-sea exchange and advection on the stochiometry of O$_2$/DIC changes, O$_2$ and DIC concentrations need filtering for the influence of non-biogenic processes in order to use the data for describing the biological factor. The correction which was done in that way allowed Körtzinger et al. (2008b) to estimate ΔO$_2$/ΔDIC slopes during spring bloom in the Labrador Sea in the range from -0.78 to -1.36.

The oceanography of the Koljo Fjord (Hansson et al., 2013), its positioning and recorded meteorological parameters indicate that the fjord is rather protected from strong winds, water masses are mainly transported above the sill level and mixing of the entire water column occurs seldom. Thus estimation of O$_2$:DIC slopes of biological processes in the Koljo Fjord, e.g. when there was a clear indication of onset of spring bloom, did not require correction for an air-sea exchange. The ΔO$_2$/ΔDIC slopes were -1.30, -1.32 and -2.08 depending on the season and the depth (Fig. 4).

We also follow a somewhat simplistic, but nevertheless effective way in separating biological and physical forcing on the carbonate system of the fjord. Fig. 5 illustrates how using the DIC vs O$_2$ plot with the axes scaled in Redfield proportions could be used to separate the processes. If curves are parallel it is likely that biological processes dominate. If they are not processes like advection/mixing and/or air-sea exchange are more important. More explicit discussion about this can be found in Paper 2.
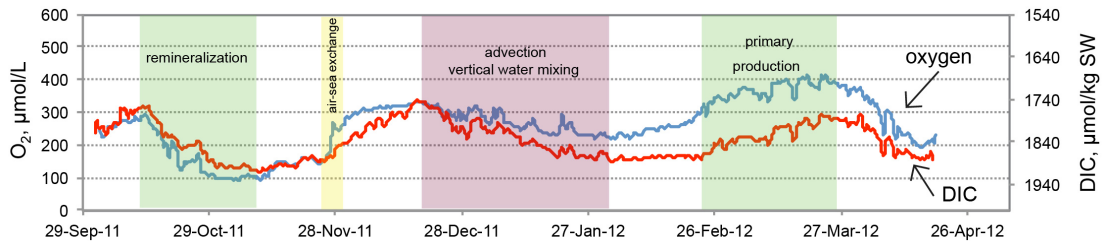
Fig. 5. Relationship between calculated low-pass filtered (>24 hours period) DIC and measured oxygen time-series at 12.6 m (2011-2012) in the Koljo Fjord. Note that DIC is plotted on a reversed scale. Unmarked periods indicate no clear dominance of a certain process.

3. Design, fluorescence detection technique and specifications of the pCO₂ optode

The newly developed pCO$_2$ sensor has inherited the basic principles and design (Fig. 6) from 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 saturation). 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 frequency and 7 mW at 1 min sampling frequency.

The detection of the signal is based on fluorescence lifetime measurements. This technique, unlike fluorescence intensity detection, is less prone to drift problems caused by bleaching or leaking of the sensing material out of the sensing foil, variations in the background light and excitation intensity.
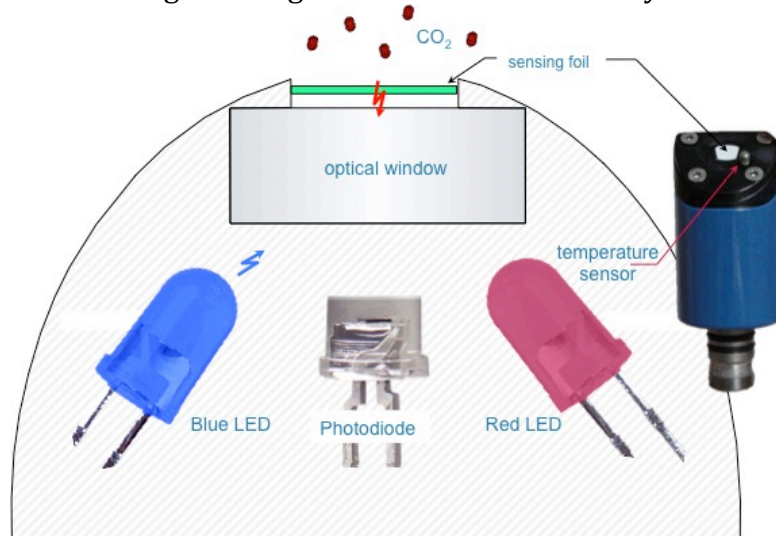

Fig. 6. Optical design and an outside view of the optode-based pCO₂ sensor.

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The sensing foils used in this thesis were developed specifically for these sensors by the company PreSens (www.presens.de). The foils 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. For a more complete description, please see Paper 1.

One of the indicators responds to changes in the surrounding pH by exhibiting a change in the intensity of blue light-induced fluorescence. A fluorescence excitation and emission spectra of the second 'reference' fluorescence indicator overlap significantly with those of the first indicator, but its fluorescence intensity is independent of pH. When the combined indicators are excited with amplitude modulated blue light, each luminophore contributes an optical fluorescence signal that lags from excitation. The longer fluorescence lifetime of the reference indicator means that the reference indicator (φ_{ref}) signal lag is longer than that of the pH indicator's signal (φ_{pH}). The combined intensity of the two fluorescence processes lags from the excitation signal by a phase φ_{DLR}, which is associated with the fluorescence lifetime of the combined indicators (Fig. 7). φ_{DLR} is dependent 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 CO_2. This measurement approach is known as Dual Lifetime Referencing (DLR) (Klimant et al. 2000; von Bültzingslöwen et al. 2002). The pCO_2 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 (Liebsch et al. 2001).
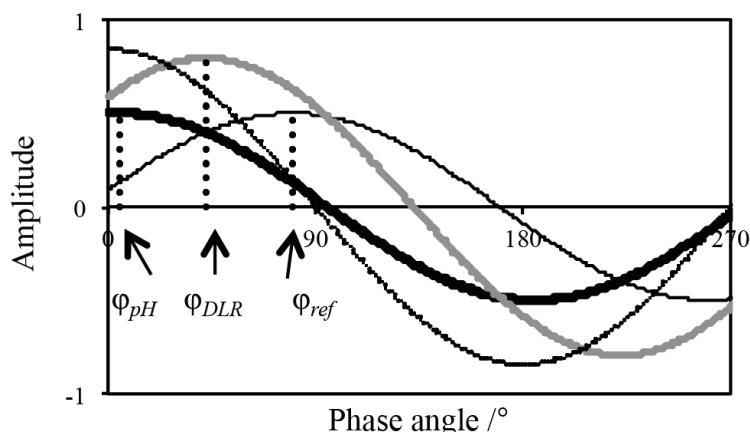

Fig. 7. The Dual Lifetime Referencing scheme: amplitude profiles for excitation light (dotted), fluorescence emission of the pH sensitive indicator (thick black), reference indicator (thin black), and the measured total fluorescence signal from the combined indicators (grey).

For the calibration procedure, pCO_2 sensors were immersed into a vessel containing 0.9% (9 psu) NaCl water solution. Normally eight (or seven) different pCO_2 levels were obtained by using mass flow controllers to mix N_2 and CO_2 gas before being bubbled into the vessel through a diffusing element.

The response time, about 5 minutes in cold water, is limited by CO_2 diffusion into the foil and is similar to other technologies.

A linear pressure effect was estimated to be 3.5% lower response in µatm per 100 bar in the lower range of pCO_2 (700 µatm), 4.4% at 3000-3200 µatm and 6% at 10000 µatm (Paper 4). The pCO_2 sensor showed similar pressure dependence as 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.

The salinity affects the response of pCO_2 sensor due to osmotic forces, which are rather slow and are in the order of days, and which drive a migration of water through the foil back and forth. The predictable error is in order of 200-250 µatm for the change from 9 psu to 33 psu.

Applications involving measurements at fairly constant salinity conditions (open ocean, most of the surface water measurements) or in highly dynamic environments, where salinity oscillates within a narrow range, will not require correction for salinity change.

A limitation of this technology is that it should not be used in sulphidic environments, because it is cross sensitive to hydrogen sulphide (H_2S). When the foil is exposed to H_2S and then is brought into normal (oxic) conditions it becomes irreversibly poisoned. The poisoning continues to increase the response signal as long as the sensor is exposed to H_2S.

The sensors have a wide dynamic range (0-50000 µatm), and size and energy consumption advantages, compared to 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.

4. Current challenges in global ocean sensing

The core Surface Ocean CO_2 Atlas (SOCAT) data set is a global compilation of underway surface water CO_2 data with 7.8 million measurements (6.3 million with fCO_2 values) from 1851 cruises run between 1968 and 2007 by more than 10 countries (Fig. 8). SOCAT brings together, in a common format, all publicly available surface ocean CO_2 data, including the Arctic and the coastal seas (http://www.socat.info).

Most of what we know about ocean chemistry is derived from limited discrete sampling and data collected from ships, which are unable to directly observe most processes on the time scales relevant to their occurrence (e. g. Outdot, 1989; Robertson et al., 1994; Watson et al., 1994). As a result, there have been few studies covering sustained (years, decades) periods with high-temporal resolution observations. Examples of such studies include the Hawaiian Ocean

Time series (HOT/ALOHA, Dore et al., 2009), the Bermuda Atlantic Time series Studies (BATS, Bates, 2007), the European Station for Time Series in the Ocean (ESTOC, Santana-Casiano et al., 2007), and the Atlantic Zone Monitoring Program (AZMP, Shadwick et al., 2011). Also smaller scale studies are described in Lüger et al. (2004), DeGrandpre et al. (2006), and Körtzinger et al. (2008a,b).
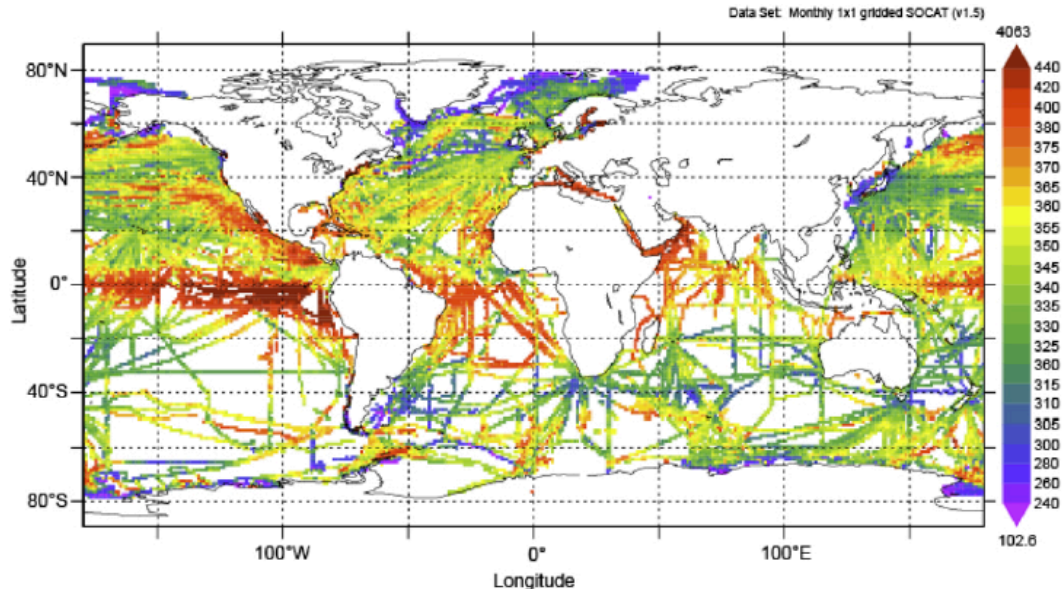

Fig. 8. Map of the mean unweighted surface water fCO2 (µatm) based on data in SOCAT database (1970–2007) as generated by the online Live Access Server. (Figure is taken from Sabine et al., 2013)

In connection with increasing atmospheric CO_2 levels, long-term pCO_2 time-series are essential to understanding if aquatic environments are sinks or sources of CO_2 (Wayne 2000; Lüger et al. 2006; Takahashi et al. 2009; Bozec et al. 2011). Both large and small scale studies of pCO_2 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 et al. 1999; Thomas et al. 2004; Kaltin et al. 2005; Wesslander et al. 2011).

Over the past decade, development of sensor technology has opened new possibilities for high-temporal resolution studies of the aquatic environment, including the carbonate system of seawater (e.g. Johnson et al., 2007). In recent years, profiling floats, which form the basis of the successful international Argo observatory, are also being considered as platforms for marine biogeochemical research (Johnson et al., 2009). Rapid progress is being made in the development of a suite of chemical and biological sensors that are low power, small in size, precise and accurate, and have long-term stability. Within the past decade, sensor technologies for e.g. oxygen, chlorophyll, particles, and nitrate have been refined. These sensors are now capable of deployment on long-endurance missions on autonomous platforms such as profiling floats and gliders. They represent the enabling technology for a global biogeochemical observing system that might operate on a scale comparable to the physically oriented Argo array (Roemmich et al., 2004, 2009). Martz et al. (2008) estimated rates of primary and export production in the South Pacific using 1.5 yr of oxygen measurements from profiling floats. Fiedler et al. (2013) showed the possibility of using

profiling floats equipped with the sensor packages as a platform for detailed and unattended observations of the marine carbon and oxygen cycle dynamics.

Technical specifications of the newly developed pCO_2 optode would make it feasible for installations on autonomous profiling floats. No doubt that low-power consumption, internal processing of the signal, and stability are the key characteristics of the sensor. A success of oxygen sensors (Tengberg et al., 2006) on Argo floats, which are designed in the similar way as pCO_2 optodes, inspires for further improvements and sensor development efforts of the pCO_2 optode. It should however be noted that the response time is at present probably too slow for profiling applications, and it is challenging to obtain an absolute accuracy which is high enough.

5. Role of sensors in mitigation actions of ocean acidification and global warming: Carbon Capture and Storage (CCS)

Carbon Capture and Storage (CCS) is a method of sequestration of CO_2 from large CO_2 sources, e.g. fossil fuel based power plants, CO_2 enriched gas and crude oil, and entrapping it into storage sites, e.g. underground in geologically suitable bedrock. This approach is regarded as one of the most important measures in the long term for reducing carbon emissions globally and it has been suggested as a mitigation to counteract atmospheric CO_2 build up and ocean acidification (Gough and Shackley, 2005; Haszeldine 2009; Wilkinson et al., 2013). According to an IEA (International Energy Agency) report in 2008, CCS technology alone has the potential to reduce greenhouse gas emission by 20 % by 2050.

For a CCS project to be regarded as a climate change mitigation activity, it is a prerequisite that the geological formations at the selected site have the appropriate long-term containment capability. These geological structures are usually depleted gas- and oil reservoirs or saline formations, which lie below the seabed. Statoil, Norway, successfully operates several CCS including Snøhvit and Sleipner (Fig. 9) gas fields since 1996 (www.statoil.se).

Fig. 9. A platform for injecting CO_2 into safe, geological storage: Sleipner, Norway. Courtesy of Statoil.

Three million tonnes of carbon dioxide are captured annually from the Dakota Gasification Company's Great Plains Synfuels Plant in the USA and transported several hundred kilometres by pipeline to the Weyburn oil field in Saskatchewan, Canada, for enhanced oil recovery and storage in a depleting oil field.

It is well established that the dissolution of CO_2 in sediment pore waters and seawater causes fundamental shifts in aqueous carbonate chemistry, lowering pH and changing the availability of key biological substrates such as carbonate and bicarbonate. Decreasing pH has been shown to mobilise potentially toxic trace metals, impact nitrogen cycling and provoke acidosis in animal tissues. Decreasing availability of carbonate at lower pH inhibits or impedes calcification and formation of shells in many classes of both plants and animals.

Proximal to a CCS derived leak, it is likely that CO_2 would reach high concentrations and significant ecological damage would occur. Early studies indicate that only persistent leaks of a significant proportion of reservoir capacities would cause widespread (>10km scale) impact (Blackford et al, 2008). However, crucial environmental aspects of such persistent or chronic leaks are currently indeterminate. For example, what are critical leak flow rates? What are CO_2–seafloor sediment interactions? What are ecosystem recovery and acceptability thresholds? What exactly is the footprint of a given leak event? Such questions need resolving before any comprehensive risk assessment of CCS can be delivered. New and significant theoretical and experimental studies in the last years, within both European Union and National programs (e.g., EPOCA, BioAcid, RISCS, NERC OA Programme) are addressing such questions. A comprehensive summary of impacts of natural CO_2 fluxes on the biogeochemical conditions is given in Kirk (2011).

Previous efforts to study controlled CO_2 releases were restricted to either small-scale direct injections of liquid CO_2 into the deep-water layers or model studies of the fate of released CO_2. Off the coast of California small scale liquid CO_2 injections were carried out in a series of experiments (Brewer et al., 2003, 2004), which later developed into the FOCE (Free Ocean CO_2 Enrichment) program (Kirkwood et al., 2005, 2009; Walz et al., 2008). Bellerby et al. (2008) studied the responses of the natural pelagic ecosystem to pCO_2 perturbation during the Pelagic Ecosystem CO_2 Enrichment (PeECE III) experiment.

The environmental experiment QICS (Quantifying and Monitoring Potential Ecosystem Impacts of Geological Carbon Storage) was carried out in Ardmucknish Bay, Oban, Scotland by the Scottish Institute for Marine Sciences (SAMS) during May-October 2012 and simulated a small scale leakage of carbon dioxide by release through a bore hole from a land-based gas-storage of CO_2. A number of water column parameters, including pCO_2, pH, oxygen, temperature and salinity, were measured as a part of multiparameter surveillance covering sediment, water column and atmosphere above the release area.

The newly developed pCO_2 optode was measuring changes in the water column during the release of CO_2 gas together with four other types of multiparameter

instruments equipped with e.g. pCO_2 ISFET-based technologies, and sensors for pH, oxygen, temperature, salinity and currents.

It was shown that purposefully released CO_2 caused tidally-induced pCO_2 oscillations in water column in the order of 20-200 µatm. Tidal oscillation can also be interpreted as short-term, acute leaks of CO_2: at high hydrostatic pressure (high tide) the CO_2 bubbling was restricted, while at low hydrostatic pressure (low tide) CO_2 bubbles were well seen (Fig. 10).
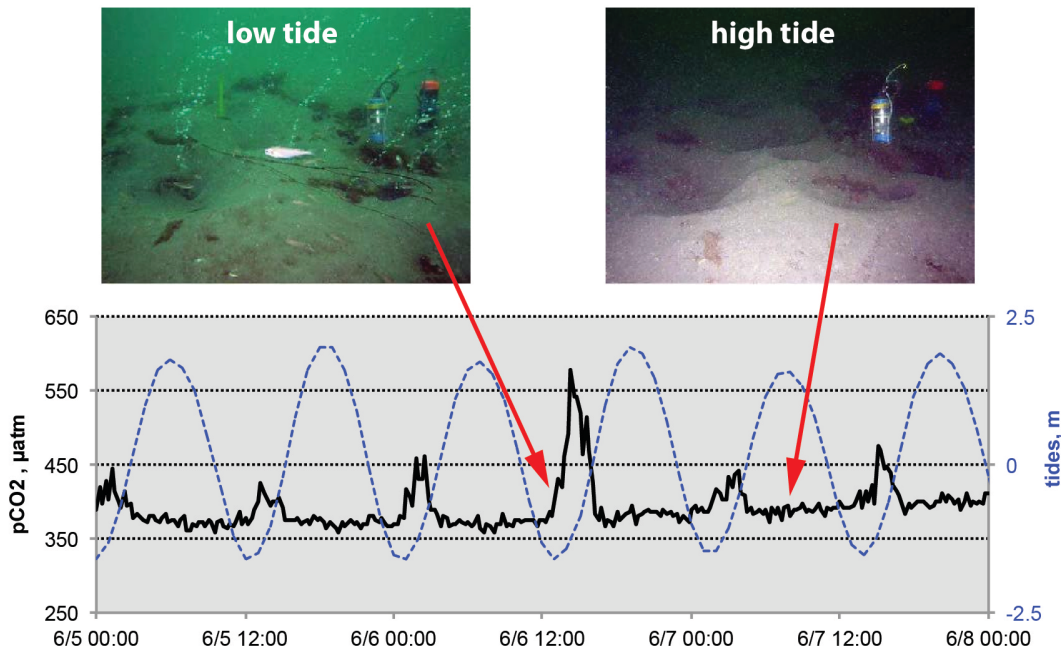

Fig. 10. Occurrence of CO_2 bubbles under low (left) and high (right) hydrostatic pressure, i.e. low and high tide, in the top panel. The chart (lower panel) represents the response of the pCO_2 sensor (black line) to the tidal cycle (blue dashed line). The pictures and the chart are courtesy of QICS.

A gradual build-up of the background level from 375 up to 550 µatm towards the end of the release period, when the gas flow was about 220 kg CO_2/day, was a result of a 'chronic' long-term leak: 4.2 t CO_2 was released over a 37-days period through a pipeline. Acidification of water column as a result of CO_2 dissolution was temporary and the recovery took 20-22 days until the system reversed to the natural, original state.

More information and preliminary results from the CO_2 release experiment QICS can be found in Paper 3. A general conclusion is that the pCO_2 sensor was effective in detection potential acute and chronic leakages related to the functioning of the CCS. Moreover, the sensor indicated that at the rates of leakages (10-220 kg CO_2/day), which were applied during QICS, a strong heterogeneous field of pCO_2 was established in Ardmucknish Bay. The implications of this study include practical guidelines on the design and construction of CO_2 monitoring/warning systems at CCS fields.

6. Advantages of multivariate statistics over classical data processing

Available smart sensor technology used in this work supplied us with unique multiparameter data that give deeper insight into functioning and characteristics of the water system of interest. However, it is necessary to establish the dependencies within the obtained multiparameter data matrix. Property-property dependencies are usually well established, like temperature effect on pCO$_2$ under isochemical conditions (i.e. fixed A$_T$ and DIC). With more than two parameters varying simultaneously and related through cause-effect links, the task does not seem easy. A multiparameter statistical data analysis or MVDA (MultiVariate Data Analysis) offers a handy and relatively easy solution to a problem of dealing with large amount of information. There are two major advantages of using MVDA: (a) it reveals complex interaction within the data matrix, which are hardly 'seen' with a classical data assessment; (b) it emphasizes significant factors in the matrix and can single out the properties, which are less significant and hence could be neglected. The latter feature is applied in multivariate calibration techniques to separate important factors and even for constructing a practically applicable calibration model (Paper 4 and Berntsson et al., 1997).

In many cases MVDA is a complimentary tool to classical data assessments, but sometimes it becomes indispensible and often uncovers the trends, usually invisible with a classical approach. A vivid example of how helpful and crucial MVDA can be is given in Paper 3.

7. Overview and future outlook

An overview of the development work and testing of the pCO$_2$ sensor, which was done over the past three years and of which all is not included in this thesis, is presented in Figure 11. It also shows the extent of the performed work.

Despite satisfactory performance that was shown by the recently developed pCO$_2$ sensor, there is still room for further improvements. Ocean acidification studies usually require very high accuracy (± 1 µatm) measurements, which remain challenging for the pCO$_2$ sensor at the current development phase. More general and comprehensive description of effects of pressure, salinity variations, and cross-sensitivity as well as of tolerance to various 'stressors' in the aquatic environment will be achievable via a series of laboratory experiments and subsequent field trials. A combination of improved accuracy with already documented long-term stability, low-power consumption characteristics, easy maintenance and integration into different platforms, e.g. buoys, moorings, observatories, gliders and floats, will make the pCO$_2$ sensor a powerful tool in the hands of scientists and opens new possibilities in describing carbon cycling in the ocean and globally.
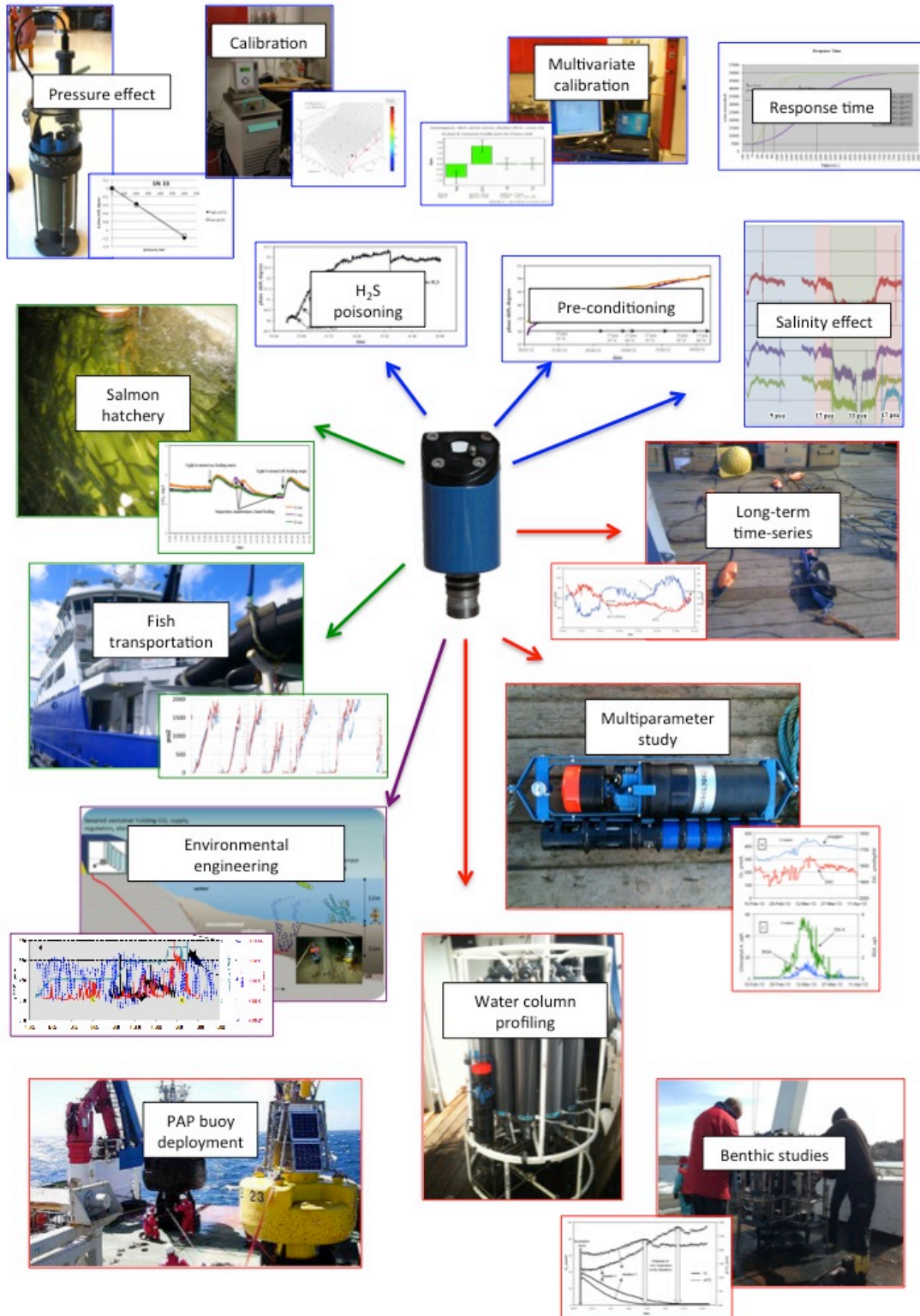
Fig. 11. An overview of the tests (marked with blue) performed during the development of the pCO₂ sensor. Biogeochemical studies are marked with red and monitoring studies are marked with purple (CCS project) and green (fish industry).
The materials are courtesy of Dariia Atamanchuk, Peter J Thomas, Jostein Hovdenes, Aanderaa Data Instruments AS, QICS project, and the managing project EuroSites at the Porcupine Abyssal Plain (PAP).

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A wide dynamic range of the sensor (0-50 000 µatm) makes it suitable also for monitoring of hazardously high pCO_2 levels in closed fish tanks or fish-transporting vehicles. On-going studies are confirming a great advantage of using the pCO_2 sensor in near real-time detection of elevated CO_2.

Future work would also include an integration of the pCO_2 sensor into available platforms for continuous monitoring and observation of the global ocean. One step ahead in better understanding the interactions within the carbonate system of seawater could be a construction of an *in situ* DIC analyser using available technologies for pCO_2 and pH sensing with subsequent calculation of DIC using known equations. Because of the important dynamic range of this sensor a system in which the water in front of the sensor foil is acidified could be envisaged. This could make it possible to measure DIC *in situ*. We are working on current and exploring new possibilities of improvement of the pCO_2 sensor to make it suitable for new major water applications.

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