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Lead beneficiary	UGOT
Lead authors	Dariia Atamanchuk, Anders Tengberg, Mikhail Kononets, Per Hall
Contributors	OGS, HCMR, ULPGC, UEA, NKE, CNR, CNRS. External contributors: Univ of Kyushu (Japan), YSI Inc. (USA/UK), Franatech (Germany), Aanderaa (Norway)
Submitted by	Sofia Alexiou

1. Background

Measurements of inorganic carbonate system species are an important part of studying the global carbon cycle and its perturbation related to the climate change, and anthropogenic impact. This report focuses on a recent field comparison exercise, which included pCO$_2$ and pH measurements, conducted by the University of Gothenburg (UGOT) in the Spring of 2014 in coastal Swedish waters. The overall objective of the study was to evaluate some of the existing sensor based technologies for pCO$_2$ and pH measurements.

WP12 RT1 within FixO^3 seeks for information on the performance of instruments that could be deployed on fixed observing platforms, like Eulerian observatories, buoys, mooring arrays, and aims to assess their field performance. Information about the quality of unattended pCO$_2$ and pH measurements on these type of platforms is limited in general and do not, as far as we know, exist for deeper waters, e.g. below 1000 m depth.

One goal within FixO^3 is to perform a longer deep-water sensor inter-comparison of the few technologies that can handle high pressure. However, before this deep water inter-comparison, an evaluation in a less risky shallow water environment was carried out at the cabled Koljo Fjord observatory, operated by UGOT, on the West Coast of Sweden. This document is reporting on the methodology and results from the latter study.

Seven research groups representing eight countries (Sweden, Spain, Japan, Norway, USA, Germany, Greece and Italy) participated in this exercise. Four different measuring principles from 5 different manufacturers participated in both pCO$_2$ and pH sensor evaluations. Since some of the sensors were duplicated a total number of 8 pCO$_2$ and 7 pH sensors were present.

Since our work in FixO^3 is on the inter-comparison of pCO$_2$ sensors, the focus of this report is such, and we use pH data only partially for quality control. The intention is to present the complete results in a scientific publication.

During the deployment fouling was significant and affected some of the sensors. Consequently the effects of fouling are also discussed.

2. Introduction

In the surface waters of the open-ocean pCO$_2$ has been occasionally measured by ship-based underway systems (ie. General Oceanics, Franatech Module for Ferry-Box). SOCAT (http://www.socat.info) serves as a storage of collected pCO$_2$ data from ferryboxes, underway systems and from manual water sampling and analysis during research cruises. Before being included in SOCAT the data passes the quality control filter and is supported by any available metafiles. As a result, SOCAT provides an

overview of pCO$_2$ distribution in the ocean on a global grid. The atlas, however, is lacking sufficient temporal resolution to monitor variations on monthly-seasonal scales.

Fixed–point observatories, on the other hand, could provide the desired resolution at particular 'hot spots' that are identified to be significant or representative for the area. The confidence in quality of *in situ* measurements, however, can barely match observations made by ship-based underway systems which include frequent calibration and checking with reference gases. Most of the known technologies that measure pCO$_2$ or pH *in situ* are power demanding and thus it's crucial to ensure constant high power is supplied either through cables or from batteries/accumulators. This requirement has to be carefully investigated since unattended deployments at remote fixed observatories can last for years. In conjunction with the previous statement, stability and endurance of the sensors seems be the foremost important aspect in achieving the desired level of data quality.

It is widely recognized that coastal areas are the most vulnerable and hence sensitive to climate change and anthropogenic impact. The direct measurements of net community production in shallow waters reveal how carbon cycling can be affected by various processes such as eutrophication, pH and temperature change, spreading anoxia, etc., which are related to climate change.

One major task of WP12 is to report on further enhancement of measuring capabilities of existing observatories by integrating suitable instruments. It was decided to approach this problem for pCO$_2$ measurements by evaluating the instruments' performance in realistic conditions of a deployment.

Inter-comparison of pCO$_2$ instruments has been performed before: the ACT demonstration evaluated pCO$_2$ instruments during shallow water coastal deployments (Tamburri et al., 2011), the JAMSTEC-NIES inter-comparing tests in 2003 and 2009 were conducted in an indoor seawater pool and a shipboard inter-comparison of underway pCO$_2$ instruments was performed onboard R/V Meteor (Körtzinger et al., 1996). The longest deployment lasted for two months; for autonomous deployment in the field batteries were used for powering the instruments/sensors and data from the instruments was retrieved only after their recovery.

The ACT endeavours were the closest to the setup in our study with respect to the technical solution, studied ecosystems, and the variety and types of *in situ* instruments. However, only four years later, a couple of new technologies have entered the market and the instruments used in ACT in 2010 have been significantly upgraded. Therefore, we took the ACT framework, adapted it according to the available infrastructure for the deployment and applied it for the instruments' package provided for the study.

3. Materials and methods

3.1 Deployment site

Planning and coordination with the partners of the inter-comparison experiment started during the FixO³ Kick-off meeting in Rome (16-18 Nov 2013). As a lead of RT1 – Enhancement of CO_2 measurements - within WP12, UGOT proposed the Koljo Fjord Cabled Observatory (www.emso.eu) as a place to conduct the experiment. A cabled observatory was installed in the fjord (58.22825 N, 11.57400 E) in April 2011 at 42 m depth, and it has been operational at this location since then. The observatory comprises of an underwater hub, to which up to four separate and independent nodes can be connected. The main measurement node consisted of a Recording Doppler Current Profiler (RDCP-600) instrument about 1 m above the seafloor and a Seaguard® current meter positioned closer to the surface, and connected to a "string" with about 30 sensors distributed vertically measuring oxygen, pCO$_2$, conductivity/salinity and temperature at multiple depth levels. The RDCP-600 was equipped with sensors for temperature, salinity, pressure/depth, oxygen and turbidity; it provided current information at 1 m resolution including the top centimeters surface current and relative particle measurements through the water column. The Seaguard® provided horizontal currents, oxygen, conductivity and temperature data from the sensors at ca 8 m from the surface directly connected to the instrument. The observatory infrastructure was manufactured by Develogic GmbH (www.develogic.de), and all instruments and sensors were from Aanderaa Data Instruments (www.aanderaa.no). Data were recorded every 30 minutes and presented in near real-time through the website: http://koljofjord.cmb.gu.se.

A FixO³ node – an inter-comparison node - was proposed to be installed at the observatory as the second node in addition to the existing one, and to function as benches for the inter-comparison.

The rationale behind using the Koljo Fjord Cabled Observatory as an infrastructure that would host the benches was the following:

- the observatory provided land power to the nodes through the cable;
- real-time communication with the observatory and data output was established and was successfully functioning for 3 years;
- the observatory was easily reached from the shore and it took 1 h to get to the site with the UGOT ship and it could be reached with a small boat in 5 minutes for more frequent reference sampling during the on-set of the inter-comparison;
- the maintenance/service of the observatory was simple and did not require additional equipment (ROV, divers, etc.). Normal recovery/deployment time of one of the observatory nodes took less than 30 minutes;

- integration of the new node would be less labour, resource and time demanding since UGOT had experience in installing and operating the observatory;
- existing sensor nodes could provide background and supplementary information during the inter-comparison;
- the general conditions have been well studied in the Koljo Fjord (Hansson et al., 2013). Conditions are variable and thus ideal for testing of new sensor technology. In the upper water column, where the test node was deployed, salinity and temperature vary by up to 10 and 20°C, respectively. Partial pressure of CO$_2$ (pCO$_2$), varies from 200-1000 µatm and O$_2$ between 50-500 µmol/L;
- the observatory is deployed at a sampling site of a monthly monitoring program run by SMHI (Swedish Meteorological and Hydrological Institution) for more than 50 years.
- fouling is an important aspect to consider during long-term deployments. The Koljo fjord waters have relatively high fouling during the active spring and summer seasons.

3.2   Preparation of the instrumental frame

It was decided that for the proposed inter-comparison to combine both pCO$_2$ and pH instruments/sensors since these parameters are closely linked through the carbonate system of seawater. During the FixO^3 Kick-off meeting the partners who attended (HCMR, CNRS, ULPGC, OGS, nke, UGOT) agreed to perform this inter-comparison in the spring of 2014 in Sweden. The deployment supported by the infrastructure of the Koljo Fjord Observatory was scheduled for two months during April-June. For this period the partners were supposed to provide pCO$_2$ and pH instruments, which they had in their possession and which would be available during the proposed time period. Based on preliminary information about availability of the instruments within the FixO^3 community UGOT took responsibility to design the set-up for the inter-comparison (see D12.1, www.fixo3.eu). It was further agreed that partners would provide the information on the sensors' specification, in order to ensure that the deployment framework was completely ready to host these sensors/instruments. To find out whether the instruments fulfilled the requirement for the deployment and whether the sensors were available, a few questionnaires were sent out. Industrial and academic groups outside the FixO^3 consortium, who were identified as potentially valuable contributors, were also contacted with a request to provide their instruments for the inter-comparison.
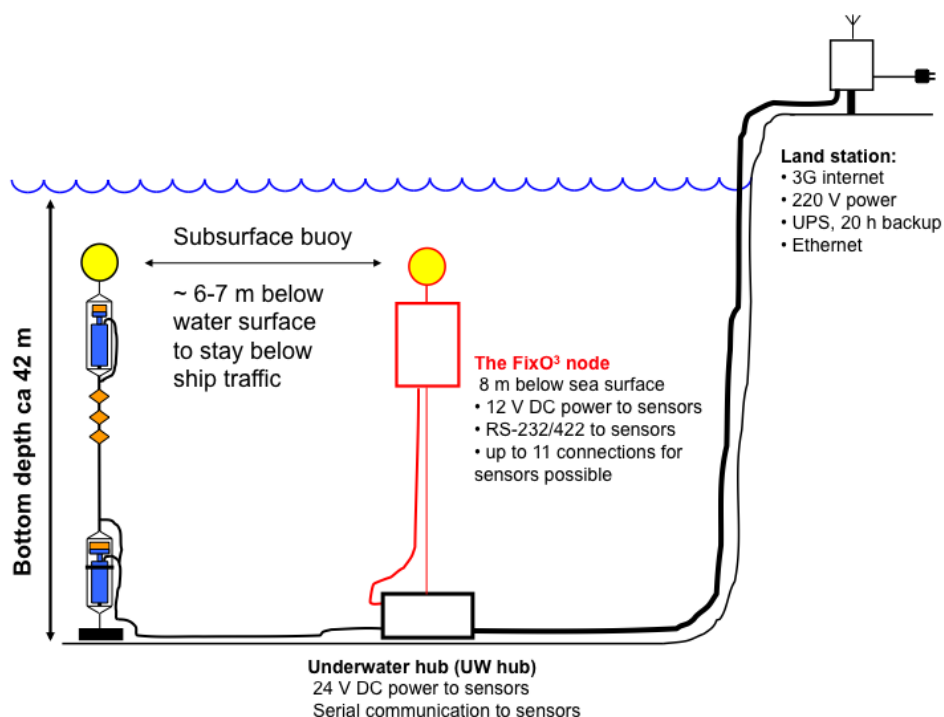
Fig. 1. The used design of the inter-comparison set-up (The FixO³ node in the drawing is on the right, and the main node of the Koljo Fjord Observatory is on the left).

3.3   Instrumentation

A total of 15 instruments/sensors became available for the inter-comparison: 4 different technologies (fluorometry, IR, ISFET-based and laser) from 5 different manufacturers for pCO2, and 4 different technologies (fluorometry, colourimetry, electrochemical and ISFET-based) from 5 different manufacturers for pH measurements.

Setup. Prior to the deployment all instruments were set-up, calibrated and the partner verified the calibration. Special cables that would allow connecting each sensor/instrument to the multiplexer were requested and obtained from the partners. The instruments that operated with external pumps, i.e. PSI Pro and PSI Pro CV with SBE 5P/5T pumps, were able to obtain power for both instrument and pump through one power line. Instruments were then programmed to record the data at the agreed measurement interval, though the interval varied between instruments due to certain limitations. The clocks have been synchronized; moreover a multiplexer was putting its own timestamp when recording the data from multiple instruments. The following

instruments were connected to the multiplexer one by one and communication and power supply was checked:

CONTROS HydroC® CO$_2$, Seaguard®, PSI® pCO$_2$ Pro CV + pump, PSI® pCO$_2$ Pro+ pump, Franatech® CO$_2$, SensorLab pH

Due to cross-talk and compatibility issues, which were not resolved at the time of deployment, Seaguard® and PSI® pCO2 Pro, were left to log the data on the internal loggers, but were receiving power from the cable.

The following instruments were left as standalone units, i.e. no data transmission, with internal data storage and power from the batteries, due to various reasons:

- **pH electrode from Univ. of Kyushu** – no serial communication was pre-arranged; can easily work on internal batteries
- **pH/pCO$_2$ ISFET** –12 VDC-24VDC power adapter was missing, can easily operate on internal batteries
- **EXO2® YSI** – arranging the on-line communication was rather complicated - hardware additions in the multiplexer were required - and it was decided to skip this; can easily operate on internal batteries
- **RCM9®** - not a part of the inter-comparison, provided auxiliary data; can easily operate on internal batteries.

Table 1 provides an overview of the deployment settings and configuration of the instruments.

Table 1- Instruments used during the Koljo Fjord inter-comparison study

Instrument	Parameter(s)	Interval	Antifouling	Sensing technology pH/pCO$_2$
Contros HydroC™ CO$_2$	pCO_2	1 min	Copper shield	NDIR
Aanderaa Seaguard®	2*pCO_2,pH,O$_2$,P,C,T	1 min	No	Fluorescence
PSI CO$_2$-Pro™ CV	pCO_2	30 min	Pumped	NDIR
PSI CO$_2$-Pro™	pCO_2	60 min	Pumped	NDIR
Franatech CO$_2$	pCO_2	1 sec	No	Tunable Laser Diode
2*pH electrode	pH	60 min	No	Electrochemical
2 *pH/2* pCO$_2$ ISFET	pH/pCO_2	30 sec	No	ISFET
EXO2, YSI	pH/ORP C/T, BGA-PC, Turb, fDOM, O$_2$	15 min	Wiper (every 6h)	Electrochemical
SensorLab	pH	15 min	No	Spectrophotometry
Aanderaa RCM9	O$_2$,C/T, P, currents	15 min	No	-

CONTROS HydroC™, **CO2-03-03-0906-01**, is manufactured by CONTROS (www.contros. eu) purchased by HCMR in 2009. CONTROS HydroC™ systems are optical, headspace-based underwater sensors for the measurement of the partial pressure of carbon dioxide (pCO$_2$). It is available for different operating depths with a maximum of 6000m. The standard measuring range is 200-1000ppm for CO$_2$ in a gas phase, but other custom ranges are available as well (up to 5000ppm). The housing has cylindrical shape and is made of titanium. The size depends on the model, typically the diameter is 90mm and the length is 500mm. Its size and weight (5.9 kg in air and 2.6 kg in water) makes it feasible for integration into various platforms. Power consumption is 0.4A in operational mode, and up to 0.7A during warm-up. Auto-restart after power outage is embedded into the software. The response time of the sensor depends of the water flow in front of the membrane, the water temperature and the pressure/depth. The actual response time as well as its change during a long-term deployment, which might be evoked by fouling, can be determined by looking at the data recorded during the flush interval after a zeroing. As a mechanical protection of the membrane and a basic anti-fouling measure a copper grating is mounted in front of the membrane. The response time is typically around 6 min (t_{63}) and 15 min (t_{90}), respectively, for water temperature around 20 °C, which is sufficiently fast for applications like e.g. buoy installations. It increases with decreasing water temperature and increasing pressure. If necessary for the application the response time can be largely improved by using a pump and a flow-head with the HydroC™. By that response times of around 90 sec (t_{63}) and 210 sec (t_{90}), respectively, are achieved.

Measurement principle: Dissolved gas diffuses from the liquid through a patented thin film composite membrane into an internal gas circuit. Therein, the concentrations are measured by non-dispersive infrared spectrometry. (More at the operational manual, page 7, 1.2.1 Measuring Principle)

Calibration of the unit CO2-03-03-0906-01*:* The sensor was calibrated by the manufacturer (factory calibration) at the end of 2011. The response of the sensor was checked prior to deployment in two ways.

- Lab: The response of the sensor was checked in different temperature/salinity/pH gradients.
- Aquaculture tank: The readings of the Contros inside the aquaculture tank was within ± 20 µatm to the CO$_2$ conc. values monitored by the tank system.

Specifications of the unit CO2-03-03-0906-01*:*

- Measuring range: from 0 to 3.000 ppm (Standard calibration: from 200 to 1.000 ppm)
- Resolution: < 1 ppm
- Accuracy: ± 1% of upper range value (as the total sum of all errors).

Antifouling protection of the unit CO2-03-03-0906-01*:* The copper plate covering the sensing element (membrane) of the instrument (see the pictures) is considered to be effective against fouling effects.

Expected endurance: Calibration is NOT required after changing the membranes or leaving the sensor in a case for a longer time. A calibration or service is recommended after 12 months of usage. Since purchasing the sensor in 2011 it was barely used.

Zero adjustment: auto zeroing on programmed intervals (ADD).

Operational notes: A warm-up time of 15-30 minutes is needed depending on the environmental conditions (water temperature) and settings of the sensor. Supports serial and analog communication.

Aanderaa pCO$_2$ optode, model 4797, SN31 and SN27, manufactured by Aanderaa Data Instruments (www.aanderaa.com). Mechanical design and functioning of these sensors are similar to Aanderaa oxygen optodes. The sensor housing is made of titanium, rated to 6000m water depth (12000 m is optional), with a diameter of 36 mm and a total length of 86 mm. This housing includes an optical/sensing part, a temperature sensor placed close to the foil, and the necessary electronics (a microprocessor with digital signal processing capacity). This design combined with a multipoint calibration provides internal data processing with temperature compensation of the signal. Power consumption of these sensors is as low as 0.004A or about 80 mW at 5 s sampling and 7 mW at 1 min sampling frequency. The measurement range of the sensor is up to 50 000 ppm. Response time ($\tau63$) is between 45 sec (at 40°C) and 4.5 min (at 0°C) in a non-pumped mode. Auto-start upon powering up is embedded into software. Sensors could be used in polled mode or output data at pre-set interval. For more information refer to Atamanchuk et al. (2014).

Measurement principle: CO$_2$ gas diffuses from the surrounding water into the sensing layer of the pCO$_2$ optode, where as a consequence the pH is modified. The magnitude of pH change is correlated to the pCO$_2$ level outside the membrane. The embedded DLR (Dual Lifetime Referencing) material exhibits a pH dependent fluorescence change, which is detected as a phase shift value of returning modulated red light. Detection of CO$_2$ is done within the sensing membrane patented by Presens (www.presens.de), which is revolutionary new from the classical equilibrator type systems where membrane serves only as a barrier and detection is performs elsewhere.

Calibration of the sensors SN31 and SN27: The pCO$_2$ optode was calibrated before the deployment at 15 points (5 pCO$_2$ concentrations and 3 temperatures) spanning 200-2000 µatm and 5-20 C using a temperature controlled water bath that was saturated

with gas mixtures of different %CO₂. The calibration is performed at a known atmospheric pressure and temperature. Thus correction for the pressure of water vapors and total pressure is performed when calculating pCO₂ set points. The signal is modeled using polynomial functions. The calibration was adjusted using *in situ* values.

Specifications of the sensors SN31 and SN27:

- Measuring range: 200-2000 µatm (Standard calibration from 0 to 50 000 µatm)
- Resolution: 2 µatm
- Accuracy : 3-5 µatm (calibration residuals)

Antifouling protection for sensors SN31 and SN27: No antifouling measures were adapted.

Zero adjustment: sensor is not capable of performing zeroing.

Operational notes: Sensor does not require a warm-up. *In situ* calibration is highly desirable due to the conditioning and osmotic effects - calibration is adjusted using one-point referencing methodology. The sensor cannot be used in the sulfidic waters. Supports serial and analog communication.

PSI CO₂-Pro™ was provided by ULPGC and is one of the first designs by Pro-Oceanus Inc, (Canada), built in 2009 and recently calibrated. The PSI CO2-Pro™ is a lightweight, compact, and versatile sensor for measuring the partial pressure of CO₂ in water. It provides three effective modes of biofouling resistance: darkness, solid copper, and high shear on the membrane surface using an external SBE water pump that also improves response rate. It is designed for in-situ pCO₂ measurement on shipboard in underway-mode, in the laboratory, and on moorings, profilers and gliders. It is available for different operating depths with a maximum of 1000 m. The standard measuring range is 0-600 ppm for CO₂ in a gas phase, but other custom ranges are available as well. The instrument features Delrin® housing (shallow version – 110 depth rating); other materials are used for deep versions. The housing is 173 mm in diameter and is 330 mm in length (without water inlet port and power/comm connectors). The weight is 5.5 kg in air and 0.4 kg in water. Power consumption is 0.45 A in operational mode with pump, and up to 1 A during warm-up. The pumped gas-transfer interface is typically supplied with water from a SBE 5T pump (3000 rpm). Time constant (t_{63}) for sample gas equilibration is about 2.5 min at low hydrostatic pressures and somewhat longer at higher pressures.

Measurement principle: PSI CO2-Pro™ instrument measures the partial pressure of CO₂ gas dissolved in water using a non-dispersive, infrared analyzer and a patented

supported tubular membrane fast transfer interface. This pumped interface provides an equilibrated gas sample to the detector and is configured to inhibit bio-fouling.

Calibration of the unit: Prior the deployment, the sensor was sent to the manufacturer for update and calibration purposes. Accuracy in the pCO$_2$ concentration of ± 2 ppm, a resolution of 0.01 ppm with equilibration time of 2.5 mins is certified.

PSI CO2-Pro™ is factory calibrated for 0-600 ppm (other ranges available by special order).

Specifications of the unit:

• Measuring range: 0-1000 ppm

• Resolution: 0.01 ppm

• Accuracy: 2 ppm for 0-600 ppm range (calibration residuals)

Antifouling protection of the unit: The gas-transfer membrane of the sensor is pumped preventing from fouling and particle deposition.

Zero adjustment: An internal zeroing feature provides a stable long-term baseline for ensuring accurate and stable measurements. When the Automatic Zero Point Calibration (AZPC) is initiated, the gas stream is routed through a pCO$_2$ absorbent to provide a zero ppm pCO$_2$ measurement. The pCO$_2$ AZPC measurement compensates for changes in optical cell performance and significant changes in environmental parameters such as gas stream temperature. The AZPC is used in determinations of ppm pCO$_2$ until a new AZPC is performed (recommended a minimum of once per day but more often where possible and especially where conditions such as water temperature change significantly).

Operational notes: The instrument can be supplied either with or without logger/controller. Programmable measurement schedule and "power saving" mode are available. To further save energy, the detector board is available in 30°, 40°, and 55°C detector temperature set points, with the choice typically at least 15 degrees above the highest anticipated ambient water temperature. The sensor will resolve its operation after power outages, however the data will be overwritten since the clock will be reset (this issue was fixed in the later versions of the instruments).

PSI CO$_2$-Pro™ CV, S/N 34-202-75, was purchased by OGS in 2014 from Pro-Oceanus Systems Inc (www.pro-oceanus.com) just before the exercise. The PSI CO2-Pro™ is a lightweight, compact and versatile sensor for measuring the partial pressure of CO$_2$ in water. It is designed for in-situ pCO$_2$ measurement on shipboard in underway-mode,

in the laboratory and on moorings, profilers and gliders. The housing has a 115 mm diameter and a length of 330 mm. The weight is 2 kg in air and 0.5 kg in water. Power consumption is 0.25 A in operational mode without a water pump, and up to 0.85A during warm-up. The flat gas-transfer interface is typically supplied with water from a SBE 5P/5T pump (3000 rpm). Time constant (t_{63}) for sample gas equilibration is about 2.5 min at 20 degrees Celcius. For more information refer to Jiang et al. (2014).

Measurement principle: The Pro-Oceanus CO2-Pro CV™ instrument operates through rapid diffusion of gas from seawater through a semi-permeable membrane to gaseous head space where pCO$_2$ is measured by a non-dispersive infrared gas analyzer (IRGA) based on a modified PP Systems SBA5 CO$_2$ analyzer.

Calibration of the unit S/N 34-202-75: calibrated against 5 known mixtures of CO$_2$ (over the instrument's calibrated range) in wet and dry air to obtain the fundamental non-linear relationship between sensor readings and CO$_2$ ppm. In addition, 4 different known mixtures of CO$_2$ were subsequently used in testing during quality control. The calibration was performed at a known detector cell pressure and temperature. The signal is linearized with a three-segment least-squares-fit to a quadratic equation. This equation provides an uncorrected CO$_2$ ppm for each raw sensor output. The correction applied for pressure is empirically derived so that it includes both the ideal gas law effect and the gas pressure broadening effect on infrared absorption. The detector has an on-board pressure sensor to measure the sample cell internal pressure. Multiplying the output of the detector in µmoles/ mole by pressure in atmospheres provides pCO$_2$ in µatm.

The final calibration for S/N: 34-202-45 was completed on March 19th, 2014 and the data were as follows:

Calibration gas	Avg. Sensor reading	Error
998.0 ppm	998.55 ppm	+0.55 ppm
881.43 ppm	886.38 ppm	+4.95 ppm
600.0 ppm	600.62 ppm	+0.62 ppm
378.67 ppm	376.54 ppm	(-2.13 ppm)
0 ppm	2.35 ppm	+2.35 ppm

Specifications of the unit S/N 34-202-75:

• Measuring range: 0-600 ppm

• Resolution: 0.01 ppm

• Accuracy: 2 ppm (calibration residuals)

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Antifouling protection of the unit S/N 34-202-75: The headspace of the sensor was pumped preventing from fouling and particle deposition.

Zero adjustment: When the Automatic Zero Point Calibration (AZPC) is initiated, the gas stream is routed through a pCO$_2$ absorbent to provide a zero ppm pCO$_2$ measurement. The pCO$_2$ AZPC measurement compensates for changes in optical cell performance and significant changes in environmental parameters such as gas stream temperature. The AZPC is used in determinations of ppm pCO$_2$ until a new AZPC is performed (recommended a minimum of once per day but more often where possible and especially where conditions such as water temperature change significantly).

Operational notes: Instrument can be supplied either with or without logger/controller. Programmable measurement schedule and "power saving" mode are available. To further save energy, the detector board is available in 30°, 40°, and 55°C detector temperature set points, with the choice typically at least 15 degrees above the highest anticipated ambient water temperature.

Franatech® CO$_2$, was kindly supplied by Franatech Inc. (www.franatech.com) for the study upon request. The CO$_2$ Sensor S/N 1384 was adapted from type 1 to fit to project interfacing and mounting requirements. The housing is depth rated down 40 m, no pressure effect on the measurements is observed. There is no temperature effect on the partial pressure measurement with the sensor. Response (t_{90}) is approx. 20min without pump at low turbulence conditions. Weight of the sensor alone is 2.3 kg, dimensions are: 95mm in diameter and 279mm in length. Power consumption of the sensor used in the study was 0.5A.

Measurement principle: measures partial pressure of CO$_2$ gas in a gas mixture, which is equilibrated with the water outside the gas permeable membrane. Detection is based on solid-state electrolyte cell. Further information is proprietary.

Calibration of S/N 1384: the sensor was factory calibrated prior to the deployment. Calibration uses wet gases at certified concentrations; the calibration parameters are then set directly in the sensor. No in-situ calibration is required.

Specifications of the unit:

- Measuring range: 0-50 mg/l

- Resolution: +-2%

- Accuracy: +- 10%,

Antifouling protection of S/N 1384: no special anti-fouling measures were taken.

Zero adjustment: Sensor does not perform zero adjustments or *in situ* calibration.

Operational notes: Instrument is supplied either with or without logger/controller. The sensor outputs the data in mg/l – conversion into ppm requires temperature measurement. The sensor continues its normal operational mode after short power outages. Power outages in the order of 24h should be avoided.

pH/pCO$_2$ ISFET sensors were brought into the exercise by Dr. Kiminori Shitashima, an external partner representing University of Kyushu, Japan. The sensors are custom-made units based on ion-sensitive field-effect transistor (ISFET) technology (e.g. Shitashima and Kyo, 1998; Shitashima et al., 2002; Martz et al., 2010) pH/pCO$_2$ sensor (Shitashima et al., 2008; Shitashima et al., 2010). The power consumption is as low as 0.002A, 0.009A in a standby mode. The pressure rating of Ti housing is 6000m, the weight is 2.18kg in air/1.4kg in water; the sensors themselves are extremely compact and light-weighted (see the photos). User programmable schedule and delayed start are available.

Measurement principle of pH units: The ISFET based pH sensor uses an ion-sensitive field-effect transistor as the pH electrode, and a chloride ion selective electrode (Cl-ISE) as the reference electrode. The ISFET is a semiconductor made of p-type silicon coated with SiO$_2$, with Si$_3$N$_4$ as the gate insulator surface that is the ion-sensing layer. In aqueous media, the interface potential between the reference electrode and the sensing layer is a function of the activity of the H$^+$ ion, i.e. pH. The Cl-ISE is a pellet made of several metal chlorides having a response to the chloride ion, a major element in seawater. The electric potential of the Cl-ISE is stable in the seawater, since it has no inner electrolyte solution. The devised pH sensor shows quick response time (τ_{90} < 1 s) with high accuracy (± 0.005 pH). The *in situ* (3000 m depth, 1.8°C) response time (τ_{90}) for detecting changes in pCO$_2$ was <60 seconds (Shitashima et al., 2013).

Measurement principle of pCO$_2$ units: The principle of pCO$_2$ measurement using ISFET-pH technology is as follows: Both the ISFET-pH electrode and the Cl-ISE of the pH sensor are sealed in a unit with a gas permeable membrane whose inside is filled with inner electrolyte solution with 1.5% of NaCl. The pH sensor can measure changes in pCO$_2$ from changes in the pH of the inner solution, which is caused by penetration of CO$_2$ through the membrane. An amorphous Teflon membrane (Teflon AF™) manufactured by DuPont was used as the gas permeable membrane.

Calibration of the units: pH units were calibrated on a total hydrogen ion scale (pH$_T$) using artificial seawater buffers (Tris and AMP) prior to the deployment. The pCO$_2$ ISFET units were calibrated *in situ* against the reference pCO$_2$ data.

Specifications of the pH units: See the references above.

Specifications of the pCO₂ units: See the references above.

Antifouling protection of the unit: No antifouling measures were adapted.

Zero adjustment: sensor is not capable of performing zeroing.

Operational notes: No warm-up is required.

pH electrodes, were brought into the exercise by Dr. Kiminori Shitashima, an external partner representing University of Kyushu, Japan. The submersible glass electrode pH sensors, model SPS-14, were manufactured by Kimoto Electric Co., LTD. Operating depth depends on a model and is available up to 5000m. Power consumption is 0.02A in the operational mode, 0.1A at peak current and 0.003A in a standby power mode. Housing is 75 mm in diameter and 300mm in length. Weight is 1.75kg in air/0.7kg in water. User programmable measuring schedule is available.

Measurement principle of pH units: pressure-balanced glass-electrode.

Calibration of the units: pH units were calibrated on a total hydrogen ion scale (pH$_T$) using artificial seawater buffers (Tris and AMP) prior to the deployment. pCO$_2$

Specifications of the pH units:

- Measuring range: pH 3.5 to pH 9.0
- Resolution: 0.001pH (0.1mV)
- Accuracy: set by calibration

Antifouling protection of the unit: No antifouling measures were adapted.

Zero adjustment/self calibration: sensor is not capable of performing zeroing.

Operational notes: No warm-up is required.

EXO2® pH electrode was kindly supplied by YSI Inc. (www.exowater.com), an external partner, for demonstration purposes. This is a submersible pH sensor, which is usually used with a variety of other sensors as a part of multi-parameter EXO2 sonde. The depth rating of EXO2 is up to 250 m depending on a housing, the dimensions of the instrument are 762 mm in diameter and 7110 mm in length. The weight is 3.6kg in air. User programmable interval and preset sampling schedule options are available. Power consumption of a single pH sensor within EXO2 is 0.01A. Response time (t$_{63}$) is >3sec.

Measurement principle of pH electrode: Glass combination electrode. EXO2 measures pH with two electrodes combined in the same probe: one for hydrogen ions and one as a reference. The sensor is a glass bulb filled with a solution of stable pH

(usually 7) and the inside of the glass surface experiences constant binding of H+ ions. The outside of the bulb is exposed to the sample, where the concentration of hydrogen ions varies. The resulting differential creates a potential read by the meter versus the stable potential of the reference.

Calibration of S/N 14C101809: The pH electrode was initially calibrated using buffers on NBS scale (the software gives an option to use only pre-set values of NBS buffers). The sensor was additionally calibrated 'on a paper' on a total hydrogen ion scale (pH$_T$) using artificial seawater buffers (Tris and AMP) prior to the deployment. This calibration was later used to convert raw data (mV and T) into pH$_T$.

Specifications of S/N 14C101809:

- Measuring range: pH 0 to pH 14
- Resolution: 0.01pH (0.1mV)
- Accuracy: set by calibration

Antifouling protection of the unit: A mechanical wiper was used to clean the sensing surfaces every 6h. In addition, a sensor guard made of copper was mounted to protect the sensors from fouling on unprotected surfaces on the sensors, those that were not wiped.

Zero adjustment/self calibration: sensor is not capable of performing self-calibration.

Operational notes: No warm-up is required. It's advisable to mount EXO2 downwards looking. Low power consumption allows for high-frequency sampling during substantial time-periods. This signal output adapter (DCP-SOA #599800) allows users to connect an EXO2 sonde to a Data Collection Platform as well as power it via an external 12 V DC source Users wire a sonde cable with lying leads into one side of the SOA and an SDI-12 /RS-232 output and power source into the other.

For the details about other instruments and sensors, which provided ancillary data, see www.aanderaa.com for SeaGuard and RCM9, www.exowater.com for EXO2 from YSI Inc. and www.koljofjord.cmb.gu.se for instrumentation on the main node of the observatory.

3.4 Deployment

All listed instruments in Table 1 were fixed on the Ti-frame with metal and plastic bands and stripes, and tape. The multiplexer was attached on the top of the frame (Fig. 2).
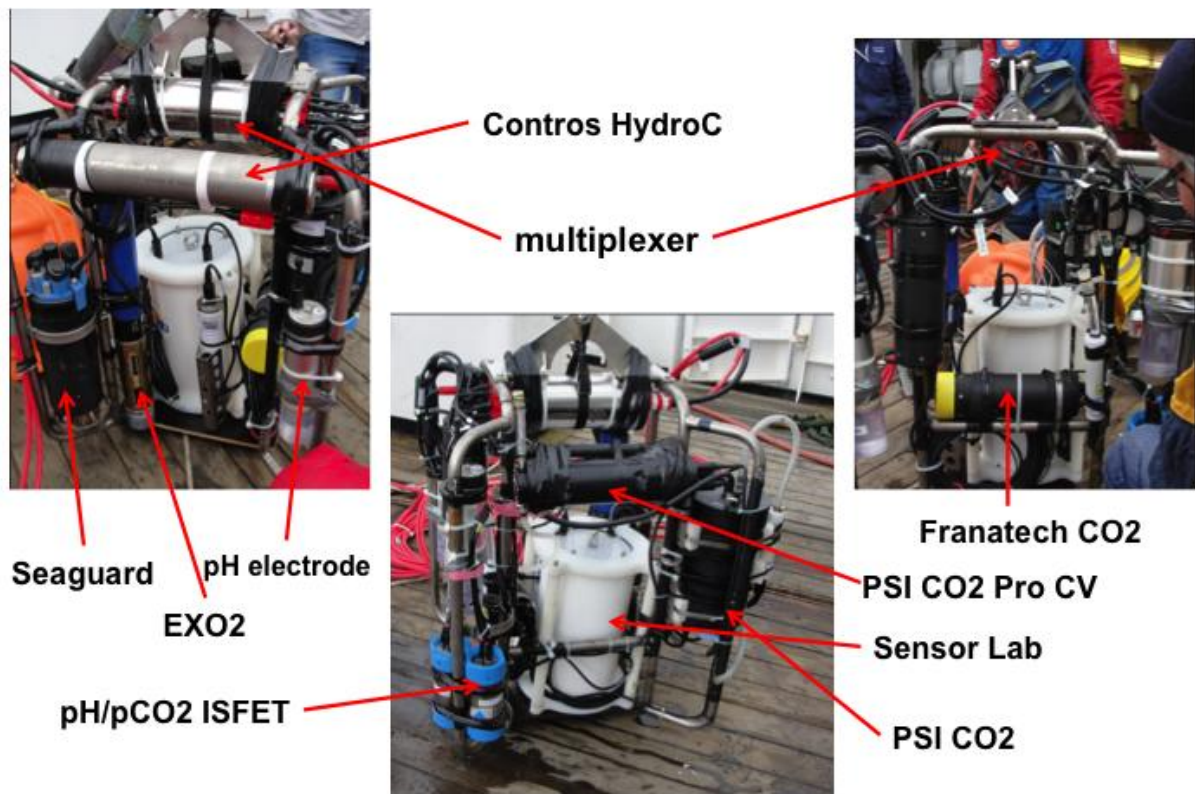

Fig.2. The FixO³ node with the sensors after assembling.

The instruments were attached in a way that the Ti frame was balanced and was not tilted when submersed in water. Due to the construction of the frame and the weight of each instrument, and the need for not having the Ti frame tilted, it was not possible to place all the instruments either on the same level horizontally or on the same level vertically. The measurement spots of the sensors and inlet of pumped instruments were placed max 30 cm apart horizontally and 50 cm apart vertically. The water volume where the sensors/instruments would measure was assumed to be homogeneous at this depth. More about the hydrodynamics of the Koljo Fjord can be found in Hansson et al. (2013).

About 1 m above the main sensors' assembly, a RCM9 multi-parameter instrument, providing measurements of currents at one level, salinity, temperature, dissolved oxygen and depth, was fitted. Further up, above the RCM9, two flotation balls were attached to assure vertical positioning of the FixO³ node in the water column (Fig. 3).

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Fig.3. Deployment of the FixO³ inter-comparison node in early April 2014 in the Koljo Fjord, Sweden. In the picture: Manolis Ntoumas (HCMR, right) and Anders Oleander (R/V Skagerak, left).

3.5   Quality control

Reference water samples were collected on: April 14, 18, 23, 28; and May 5, 9, 15, 20, 23 and 30 on the site. Water samples taken at 8 m with messenger triggered Niskin bottle – this depth was calculated from the length of the rope that was attached to the frame on one side and anchored to the bottom on the other side, and from the bathymetry data. Samples for DIC and TA were filtered through 40 µm pore filter shortly after collection. Samples were transported in glass bottles, put in a cool container, to the lab and analysed within 4 hours. Samples for pH were not filtered.

Methods:

For pH: spectrophotometric detection using m-cresol purple as an indicator; pH electrode calibrated vs. spectrophotometric system. Precision for the spectrophotometric method was 0.0015 pH units, and 0.009 pH units for electrochemical. First 7 samples were analysed using spectrophotometric detection; the last 3 were analysed through measurement with pH electrode.

For AT: AT was measured by potentiometric titration of the bottled samples according to Haraldsson et al. (1997). The titration system gave a precision in order of ± 2 µmol/kgSW. No correction for potential contribution of organic alkalinity was made.

For DIC: Determination of DIC was performed by acidification of the samples and stripping with N$_2$ gas, and analyzing the resulting CO$_2$ gas with a LiCOR instrument, model Li-6262, LI-COR Inc. The precision of the DIC measurements was ± 2-3 µmol/kgSW.

An absolute accuracy of the DIC and AT of ± 2-3 µmol/kgSW for both parameters was obtained by regular calibrations against Certified Reference Material (CRM) supplied by A. Dickson Laboratory, Scripps Institution of Oceanography, USA.

The pCO$_2$ was calculated using the set of constants from Lueker et al. (2000). Nutrients were not measured so were not included into calculations.

Only during the recovery it became clear that the FixO^3 node with the sensors was placed at 4.5 m depth – data showing this were obtained from the pressure sensor on the SeaGuard instrument. Only a few of the water samples would be representative since the water column was stratified, and conditions at 4.5 m and 8 m differed. For this reason we have also used a secondary reference standard: pCO$_2$ was calculated from *in situ* pH recorded by EXO2 pH electrode and salinity-derived alkalinity (A$_{Tsal}$) using a relation previously reported for the fjord: AT=58.78*sal+589.4 (unpublished data). Salinity data for this approximation was taken from the EXO2 conductivity sensor.

4. Results/evaluation

4.1. Data recovery

Due to various reasons not all the measurements by the instruments were performed and not all the data were recovered. Some of the failures were instrument related, while others were due to power outages/communication problems.

For merit of this study it should be mentioned that the team struggled to arrange on-line communication with the FixO[3] node. The difficulties were explained by underestimated amount of work needed to establish stable link between the data streams and the multiplexer, and between the multiplexer and the UW hub. As a result, no telemetry was available, which impeded the team from taking necessary actions when any faults occurred. Power supply, however, was successfully coming through.

There were a few occasions of power cuts:

- April 9 (07.36-15.15),
- April 26 (14.08-15.16),
- April 29 (18.53)-April 30 (00.09),
- May 2 (16.47-18.10, 18.47-19.53, 20.03-20.57),
- May 2 (23.12)-May 3 (00.13),
- May 5 (13.03-13.58, 15.13-16.08),
- May 7 (21.25) – May 12 (17.40),
- May 16 (01.53) – May 20 (20.44),
- May 26 (03.51-09.46)

Thus, some instruments, which were depending on external power, did not operate during the above indicated time periods. Power disturbances also caused erroneous data recordings by the multiplexer. We calculated a data retrieval rate (%) as a fraction of recovered data from a potentially possible volume excluding the periods of power outages.

Data Recovered:

SensorLab pH – 0%, no data were recorded. The turbid waters of the Koljo Fjord caused clogging of the inlet tubing, which has caused leakage and failure of the instruments to operate in its usual manner.

CONTROS HydroC® CO2 – 100%, the gaps in the data correspond only to power outages.

Aanderaa CO$_2$ optodes – 100%, were connected to a self-powered Seaguard®

Aanderaa pH optode – 100%, was connected to a self-powered Seaguard®

PSI™ pCO$_2$ Pro CV – 100% of the data retrieved, no gaps

PSI™ pCO$_2$ Pro – 27% of the data retrieved, data were overwritten after each power outage, hence only the last stretch of the deployment was recorded properly.

Franatech® CO$_2$ – 50% of the data retrieved, power outages caused faulty recording of the data by multiplexer; unfortunately instrument was not equipped with an internal memory.

pH electrodes from Kimoto Electric Inc, LTD – 100%, self-powered standalone units

pH ISFET - 100% and 73%, self-powered standalone units.

pCO$_2$ISFET – 100% and 73%, self-powered standalone units.

pH electrode from YSI - 100%, were connected to a self-powered EXO2

4.2. Quality control points

According to the temperature data in the fjord at 4.5m recorded by the FixO^3 node and at 8 m recorded by the main observatory node, only a few of the reference points were chosen as representative (see Fig.4). We assumed that a small temperature gradient between the depths would result in a well-mixed layer making the reference pCO$_2$ data calculated for 8m also representative for 4.5 m depth.

It was decided to choose daily midnight and mid-day values of pH from EXO2 and salinity (and derived A$_{Tsal}$) for the calculations of secondary pCO$_2$ standard.

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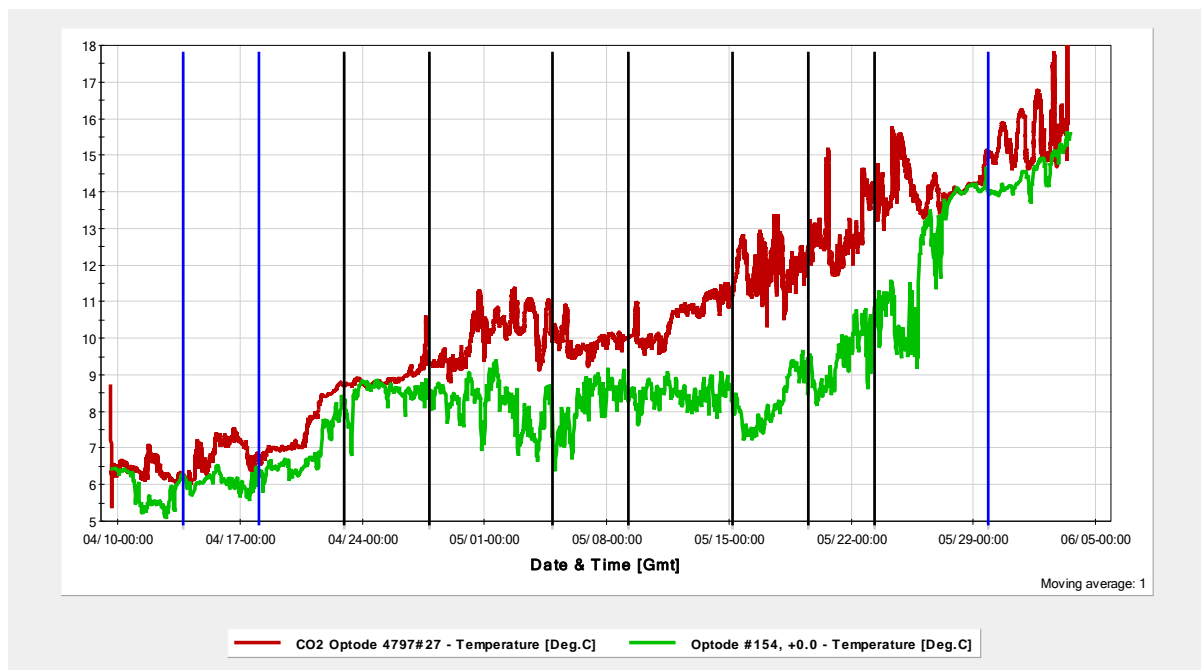
Fig.4. Temperature profile at 4.5 m (red) and 8 m (green) depth in the Koljo Fjord for the period April the 4th – June the 6th, 2014. Vertical lines indicate the water sampling occasions; blue vertical lines indicate the dates, at which the reference data were usable, i.e. when there was a small or no temperature gradient.

4.3. Results: pH and pCO$_2$ data

Summary of the results is given in a series of plots below.

The pH data from the electrochemical pH (Kimoto Inc and EXO2) sensors seems to agree rather well with each other within ±0.02-0.03 pH units for the first two weeks of the deployment (Fig.5, blue, green and red lines). After that the unprotected from fouling electodes A and B started to show higher amplitude of daily variations. The ISFET sensors seemed to follow the trend shown by the electrochemical units, but also got heavily fouled after two weeks in the highly productive waters of the fjord (see below for the photo report). The ISFET data would absolutely benefit from better calibration using data from electrochemical sensors as a reference (work is in progress). Aanderaa pH optode data were not included in the plot: the sensor drifted over time resulting in unrepresentative data.

Offset between the reference values (yellow circles) and the EXO2 electrode (red line) at three occasions was 0.009, 0.065 and 0.01, pointing on rather trustworthy pH data recorded by EXO2.

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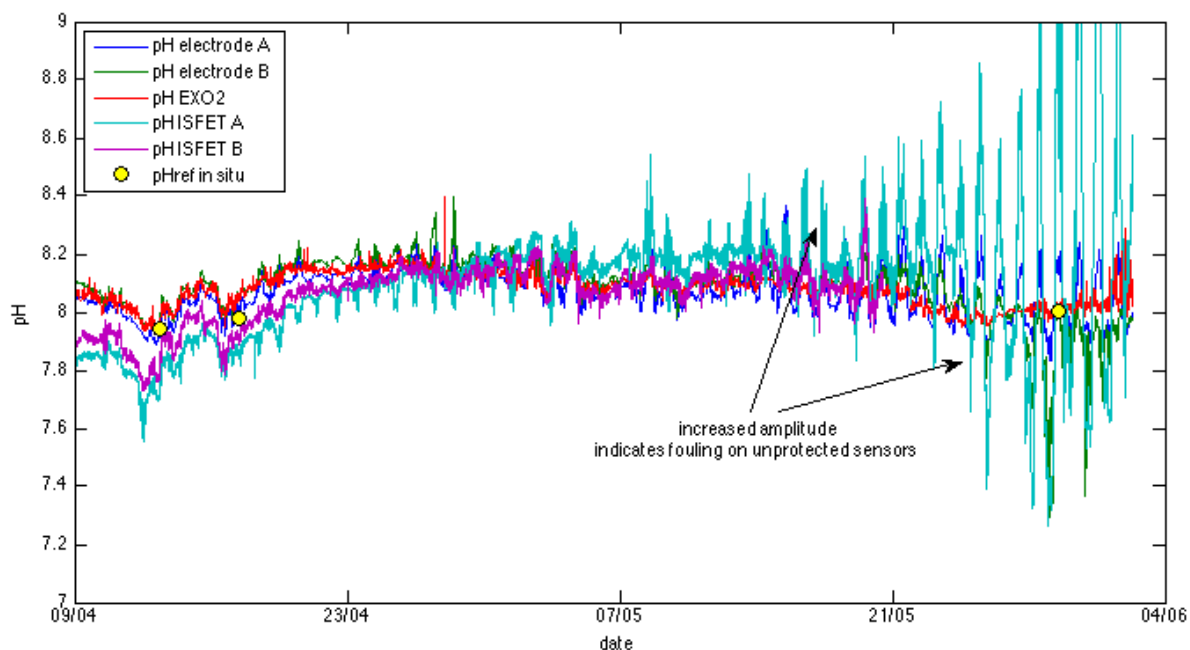
Fig.5. Overview of the pH data.

CONTROS HydroC™, CO2-03-03-0906-01.

CONTROS HydroC™ data were averaged over 15 min (Fig.6a). Gaps in the data were due to power cut-offs and were not related to the sensor performance. The sensor demonstrated good tolerance towards fouling and only the last 10 days of data indicated fouling on the membrane surface. An offset between the measured and calculated values is shown in Fig. 6b.
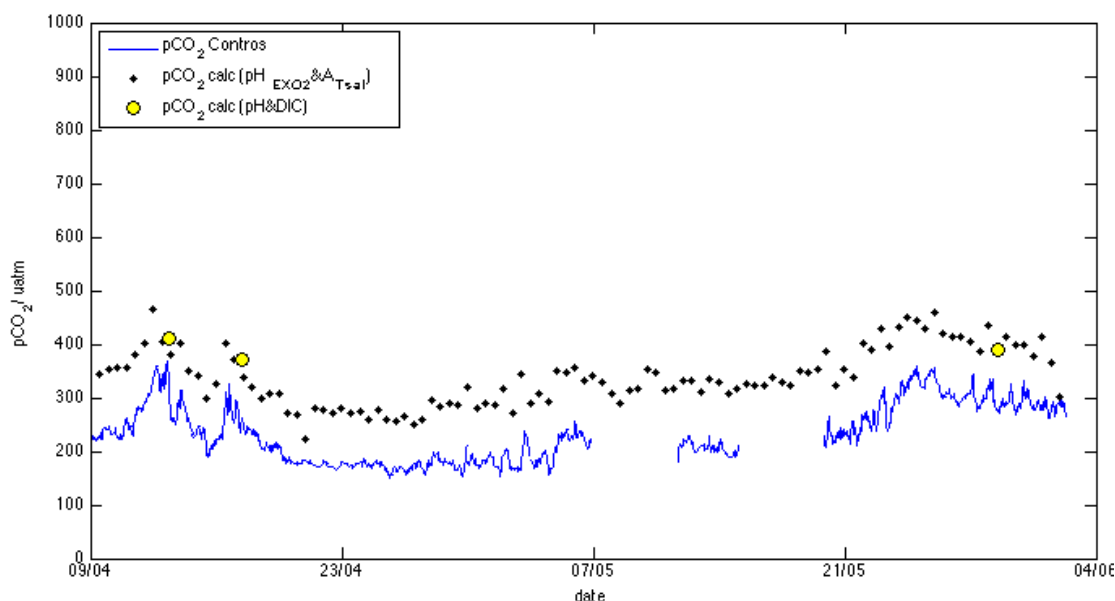
Fig.6a. Overview of pCO₂ data recorded with CONTROS HydroC™.
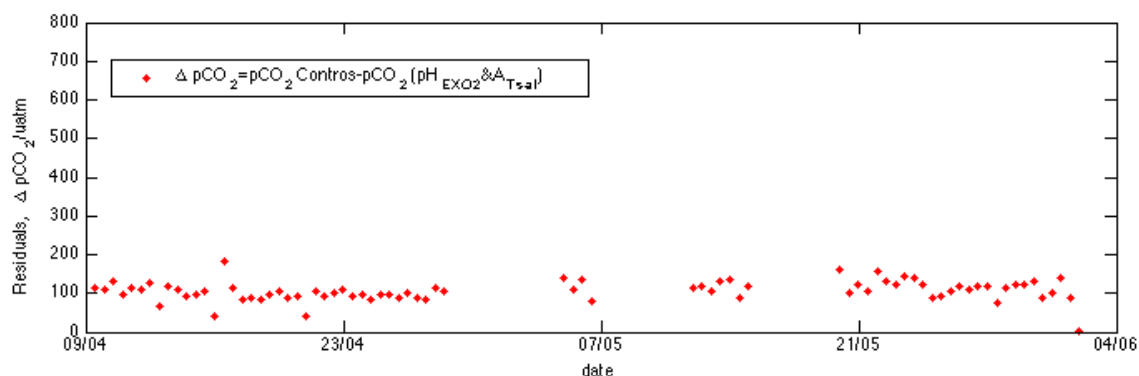
Fig.6b. The difference between the instrument values and the calculated values.

Aanderaa *p*CO₂ optode, model 4797, S/N 31 and S/N 27.

Data collected with optodes S/N 31 and S/N 27 were averaged over 15 min (Fig.7a) The two sensors agree well for the first two weeks (see Fig.7a, inset), however it looks like S/N 27 shows higher dynamics or insufficient temperature compensation – both are related to calibration. Being deployed unprotected and upwards looking the sensors experienced significant accumulation of biomass on the sensing surfaces (see the photo report). An offset between the measured and calculated values varied significantly (Fig.7b).
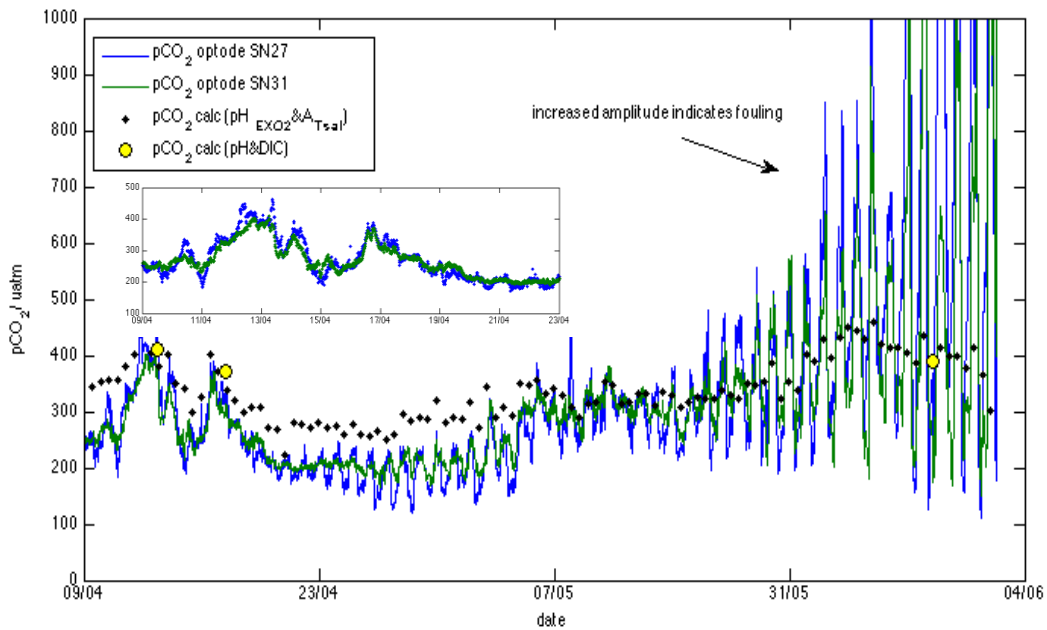
Fig.7a. Overview of pCO₂ data recorded with Aanderaa pCO₂ optodes. *The insert is a blow-up of data from the first part of the measurement campaign.*
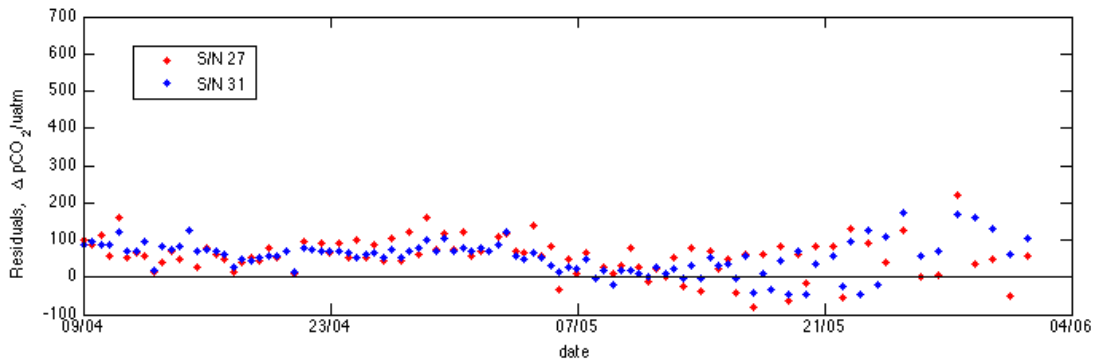
Fig.7b. The difference between the instrument values and the calculated values.

PSI CO₂-Pro™ and PSI CO₂-Pro™ CV, S/N 34-202-75

Figure 8a shows the data collected with PSI CO₂-Pro™ (60 min interval) and PSI CO₂-Pro™ CV, S/N 34-202-75 (30 min interval). There are evidences that PSI CO₂-Pro™ was collecting data throughout the deployment, not only during the last 7 days. However, overwriting of the data with each power recycling made it either unavailable or unrecognizable. The two sensors instruments tracked each other within 10-20 µatm

(Fig. 8, inset). The PSI CO₂-Pro™ CV delivered a full dataset, while PSI CO₂-Pro™ recorded only the last week of data, both with no evidence of fouling. An offset between the measured and calculated values is shown in Fig. 8b.
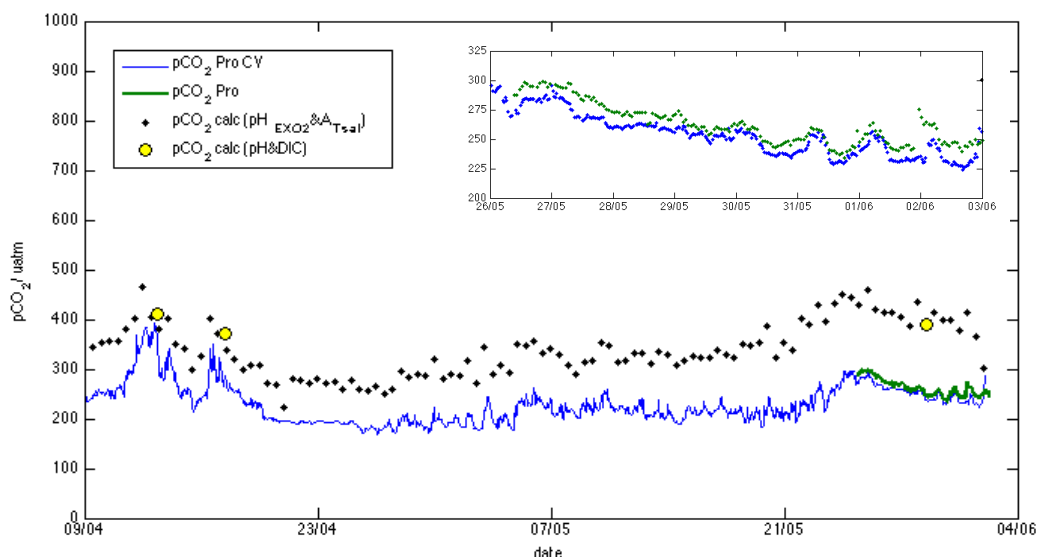

Fig.8a. Overview of pCO_2 data recorded with PSI CO₂-Pro™ and PSI CO₂-Pro™ CV. The insert is a blow-up of data from the last part of the measurement campaign.
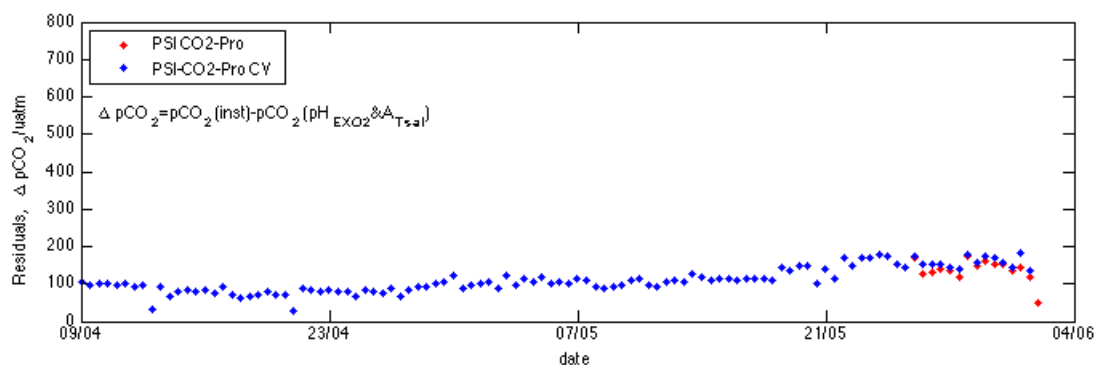
Fig.8b. The difference between the instrument values and the calculated values.

Franatech® CO₂, S/N 1384

Data collected with Franatech® CO2 were averaged over 15 min (Fig.9a). The sensor did not measure gas pressure, thus data are presented in ppmv units. The gaps in the data is due to power cut and faulty data recording within the FixO³ node, which are not related to the sensor performance. The mentioned problem is solved by equipping the sensor with its own logger; this option is offered by the manufacturer. During the

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first 4 weeks of deployment the Franatech® CO2 showed no evidence of fouling on the sensing surface, e.g. no enhanced daily pCO$_2$ cycles, despite the fact that the sensor had no anti-fouling protection. The sensor was mounted horizontally (see the photo report), which most likely prevented from deposition. Upon recovery a thin biofilm was visually detected on the sensing surface. An offset between the measured and calculated values is shown in Fig. 9b.
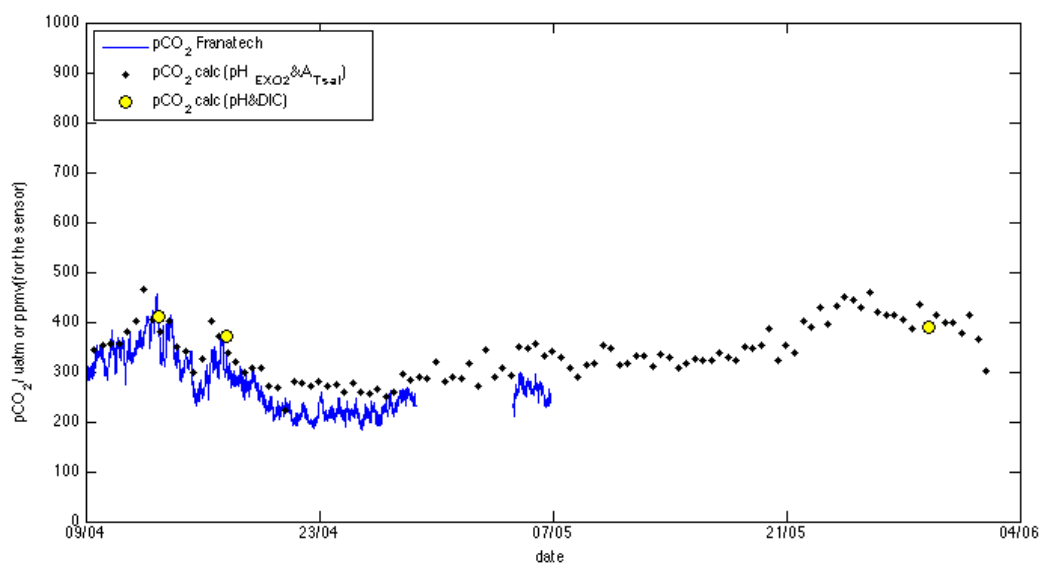
Fig.9a. Overview of pCO₂ data recorded with Franatech® CO2.
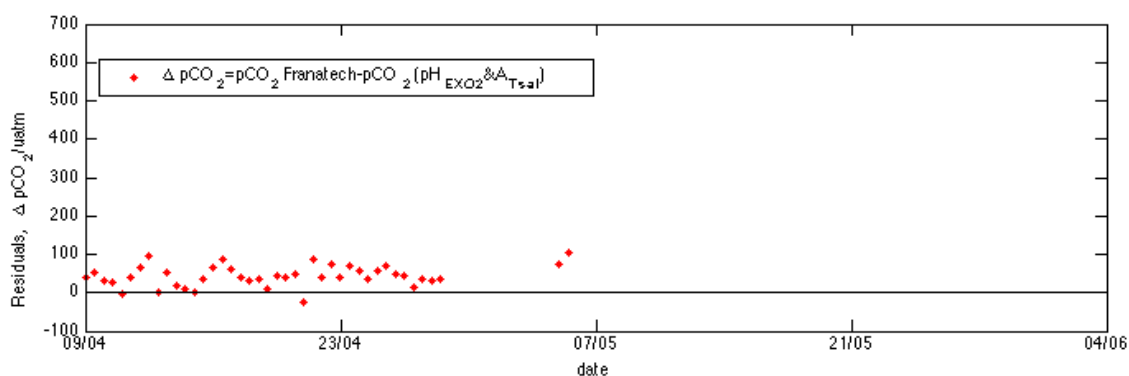
Fig.9b. The difference between the instrument values and the calculated values.

pCO₂ ISFET sensors A and B

Data collected with pCO_2 ISFET sensors A and B were averaged over 15 min
(Fig.10a). Unfortunately, sensor B was not working properly. Sensor A, however,
delivered a full dataset. Sensor A was calibrated against calculated values from water
sampling and EXO2 sensors and showed its ability to hold this calibration (see Fig. 10b).
After two weeks of commencing the measurements sensor A experienced fouling which
compromised the quality of data recorded thereafter. An offset between the measured
and calculated values is shown in Fig. 10b.
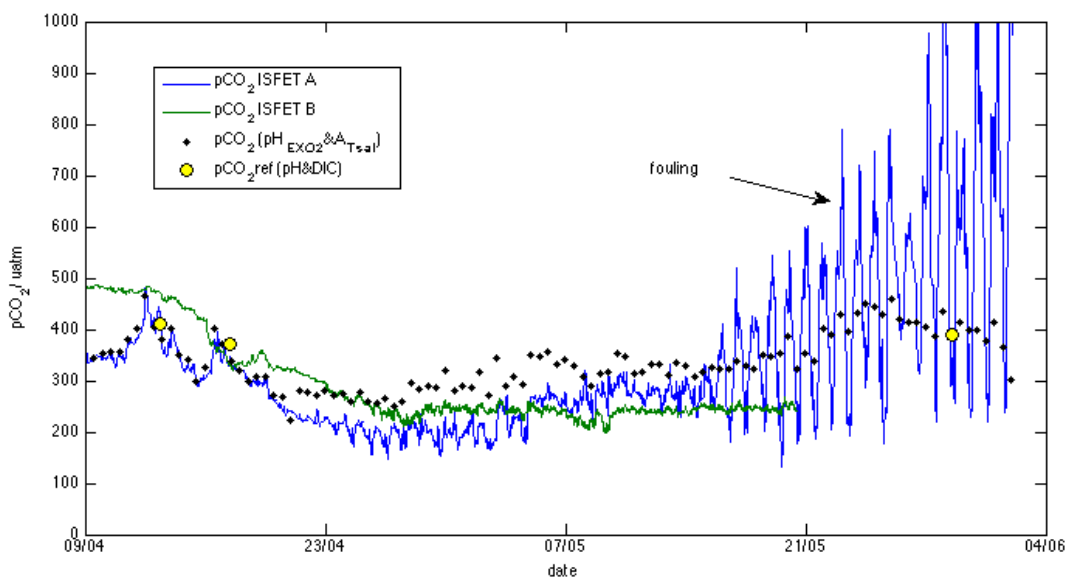
Fig.10a. Overview of pCO₂ data recorded with pCO₂ ISFET A and B.
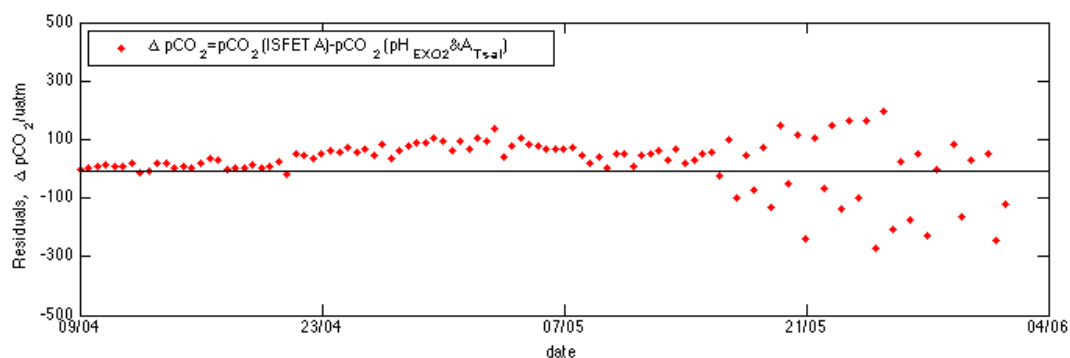
Fig.10b. The difference between the instrument values and the calculated values.

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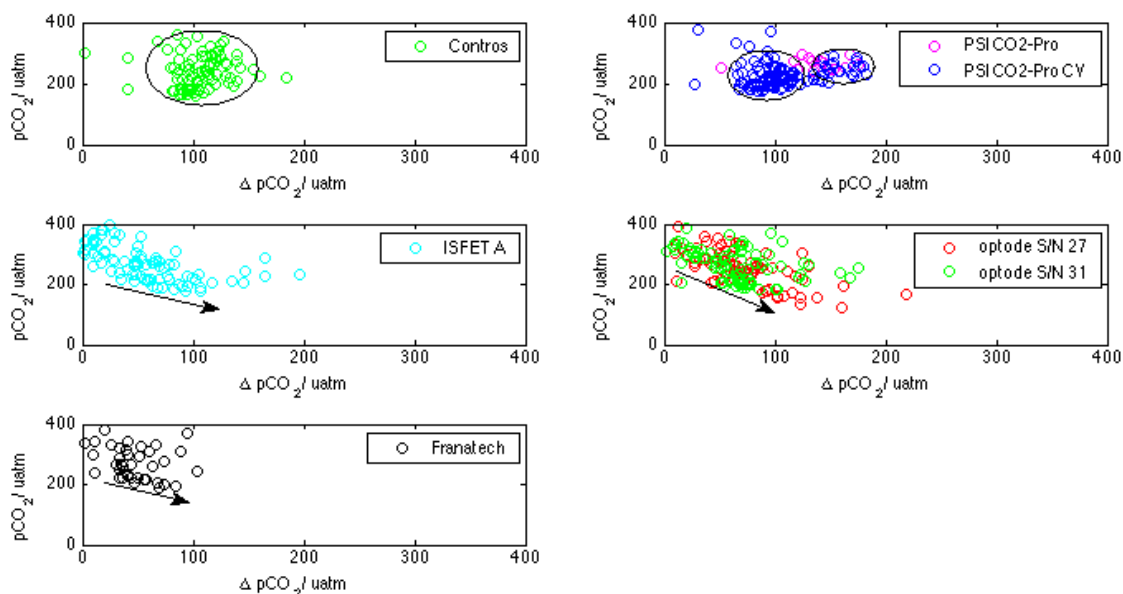
Fig.11. Summary of residuals for all sensors.
- The top two plots are CONTROS HydroC™ and PSIs™, which had antifouling protection, - hence residuals are more grouped.
- The remaining sensors (ISFET, optodes and Franatech) did not have any anti-fouling - thus there is a drift in residuals showed by the arrows.
- In general the calculated values from pH EXO and A_{Tsal} are higher than they need to be, because three independent calibrated sensors (the PSIs™ and CONTROS HydroC™) showed similar offset values.

5. Discussion and Conclusions

An adequate understanding of the aquatic carbonate system requires high quality in-situ measurements with sufficient temporal and spatial resolution. Within the frames of the ongoing FixO^3 project, and as a pre-study for a deep water fixed observatory deployment, 8 different technologies to measure pCO$_2$ and pH were compared in-situ using the Koljo Fjord cabled observatory (https://www.youtube.com/watch?v=0M9Z8BWzrkA) as the backbone. Here we report mainly on results obtained from the participating pCO$_2$ sensors. The performance of these can be summarized as follows:

- PSI™ CO$_2$-Pro CV, PSI™ CO$_2$-Pro and CONTROS HydroC™ show an offset, consistent for all three sensors, between the measured and calculated values. Note that PSI™ CO$_2$-Pro CV and PSI™ CO$_2$-Pro were newly calibrated.

- Somewhat variable offset for the data from the optodes, which increased upon fouling, and for the Franatech data.

- The pCO$_2$ ISFET showed very small offset during the first two weeks – the sensor was calibrated using the same reference data. The offset increased upon fouling.

- There was no indication of fouling on PSI™ CO$_2$-Pro CV and PSI™ CO$_2$-Pro, and little fouling on CONTROS HydroC™ at the end – all three had antifouling protection.

- The unprotected sensors (ISFET and optodes) showed 2 weeks of endurance during the productive season. After two weeks, fouling on the sensors/sensor surfaces caused high amplitude daily oscillations.

We faced several challenges when organizing this sensor inter-comparison. The fjord environment is dynamic with significant variations, which are an advantage when comparing the response of instruments, but makes it difficult to collect representative water samples for referencing. The reference samples collected in this work serve well as an approximate accuracy check, but cannot be used to single out which instruments have the highest absolute accuracy.

Biofouling in the fjord affected several of the sensors after some weeks. Until then all the pCO$_2$ sensors that participated in this exercise tracked well with one another. How and when biofouling affects the measurements and the individual sensors locally, and the mooring frame where the sensors were mounted "regionally", is a relevant data quality question for all observatories deployed in environments with significant fouling. We have from this inter-comparison a unique material that will make it possible to determine when sensors are affected by direct fouling on the sensor itself and when locally protected sensors are affected by changes in the surroundings due to fouling on the frame to which the sensors were mounted. Some of the sensors were pumped delivering water from the surroundings. The readings of those were probably not affected by biofouling, even when occurring on the frame. It is our intention to work further with this material, and present the detailed results from the pCO$_2$ and pH sensor inter-comparison and effect of fouling in a scientific paper.

To summarize, an extensive pCO$_2$ and pH sensor inter-comparison has been successfully carried out that served the purpose of both comparing the performance of established techniques as well as comparing these with new emerging technologies. There was significant involvement in this work by external and industrial participants. This exercise provided important information on the effects of fouling and it served as an important pre-study to carry out the first deep water pCO$_2$ sensor inter-comparison within the frames of FixO^3.

6. Acknowledgements

Annex I (Photo report)
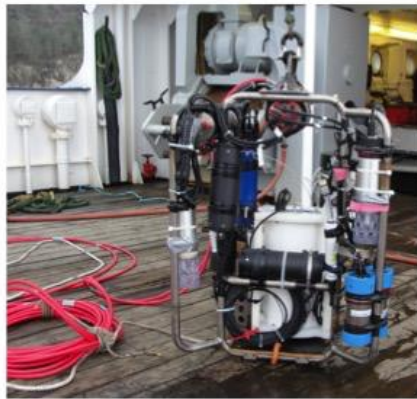
The following pictures show the sensors and frame after the deployment – focusing on fouling issues.

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Instruments upon recovery

Contros HydroC

ISFET pH/pCO2

after cleaning

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Instruments upon recovery

Franatech CO2

PSI Pro CV

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Instruments upon recovery

PSI Pro

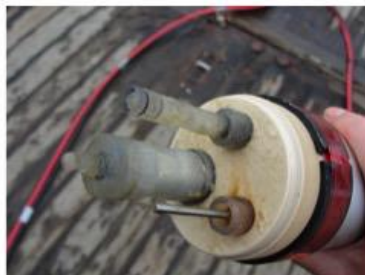### SensorLab

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Instruments upon recovery

RCM9

pH electrode – Kochi Univ./Kyushu Univ.

www.gu.se

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