Work Package 12
RESEARCH AND DEVELOPMENT ON CRITICAL OBSERVATORY FUNCTIONS

Deliverable 12.3
Long Term Deployments

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1. INTRODUCTION

This work packages has two main objectives:

1. To enhance the capability of the FixO³ infrastructures for high quality observations
2. To develop of new low energy consuming platform design in order to promote more sensors per platform and extension capacities
3. 

The first objective was addressed in detail in the FixO³ Handbook of Best Practices. In this, different aspects of operating and servicing observatories were addressed including how to maintain high data quality of sensors including the following parameters: Pressure, Temperature, Conductivity/Salinity, Currents, Oxygen, Chlorophyll-a, Nitrate and pCO₂.

The second objective has been addressed by comparing performance, including energy consumption, of different technologies in the field. The most ambitious example of this was the pCO₂ and pH sensor inter-comparison that was done in the Koljoejford (Deliverable 12.1 Sensor and testing benches for inter-comparison) and continued at the Antares deep-water site. Within the frames of FixO³ low energy multi-parameter systems were deployed in the Adriatic Sea at E2-M3A (TNA-COMBO) and at Antares (TNA-Test of pH and pCO₂ sensors in deep-sea conditions). Recoveries of systems from both sites are expected during the first six months of 2017.

Since 2011 in the Koljoejford (part of the EMSO network http://www.emso-eu.org/site/ocean-observatories.html) there has been continuous development of low power, long-term stable, deep sea rated sensors technology and methods to maintain high quality in the field. Developed and tested technologies include pCO₂ optodes (D 12.1), pH optodes (D12.5), O₂ optodes, Inductive Conductivity/Salinity Sensors, Ultrasensitive Wave/Tide sensors, Low power acoustic current sensors (Broadband and Narrow band) and low environmental impact antifouling methods.

In this Deliverable we shortly summarize the work done in this context in FixO³ and give another relevant example.
2. RESULTS

2.1 FixO³ sensor inter-comparisons in shallow and deep water (Antares)

One goal in FixO³ is to perform a longer deep-water pCO₂ sensor inter-comparison of the two technologies, pCO₂ optodes and ISFET based sensors, which can handle high pressure without special modifications. This work was started in June 2016 by deploying a mooring, at 2500 m at the IFREMER Antares site. This mooring carried an Aanderaa SeaGuard multisensor platform with a pCO₂ optode included, and two ISFET based pCO₂ sensors from Tokyo University (Fig. 1).

Before this deep-water deployment a pre-evaluation was carried out in the form of a two-month inter-comparative deployment at shallow water at the cabled Koljoeffjord observatory, operated since 2011 by the University of Gothenburg, on the West Coast of Sweden (http://koljofjord.cmb.gu.se). FixO³ deals with underwater platforms hence we did not include any technologies that are limited to deployments from surface platforms (buoys and land based stations).
Overall the deployment included 14 different pH and pCO₂ sensors. The table below lists and compares the pCO₂ sensors that took part in this test. In the figure below the mooring frame that carried the sensors is described and further below some examples of results are given. A detailed report comparing the different sensors with reference data is available as a separate FixO³ report (D12.2 report).

To summarize the test for the pCO₂ sensors, there was important fouling of the frame at the end of the deployment, which affected the sensors that were not equipped with antifouling protection. Due to power cuts there were gaps in the data from some of the more power hungry sensors that were dependent on power from land. Before fouling affected the sensors they all displayed similar relative variations in this dynamic environment with natural pCO₂ oscillations from about 200-500 µatm (see data examples below).

None of the sensors was consistently agreeing with the reference data that was obtained from frequent water samples during the deployment (see data examples below). Therefore it is not possible to judge which sensor(s) were the most accurate in absolute terms. The NDIR based sensors had better initial calibrations but when the Optodes and ISFET sensors were adjusted with the first reference value they gave similar dynamic changes and noise level (precision).

Sensors with pumps, two NDIR sensors from PSI, can normally not be sampled with the same frequency as the other sensors and the readings from the pumped sensors seems reflect a larger water volume since water is drawn from the surroundings. This was more visible at the end of the deployment when the un-pumped sensors were more affected by local fouling on sensors and the mooring frame.

The response time of the tested sensors is relatively slow, t₆₃ around 5-6 minutes which makes them challenging to use in applications where a fast response is required (e.g. for profiling).

Power consumption can be a serious impediment to longer deployments if reliable land power is not available. The optode (pCO₂) and ISFET sensors consume about 100 times less power than the other technologies.
Table 1 - pCO$_2$ Instruments used during the Koljo Fjord inter-comparison study

<table>
<thead>
<tr>
<th>Instrument; Sensing principal</th>
<th>Parameter(s); Internal ref; $t_{63}$ response time</th>
<th>Interval; pump; Antifouling</th>
<th>Internal bat; Power consum</th>
<th>Data recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contros HydroC$^{TM}$ CO$_2$; NDIR</td>
<td>pCO$<em>2$; Yes 0 value; $t</em>{63}$=6 min</td>
<td>1 min; No; Cu Shield</td>
<td>No; 5-8 W</td>
<td>100 %, small gaps due to power cuts</td>
</tr>
<tr>
<td>Aanderaa Seaguard®; Optode</td>
<td>$2^*p$CO$_2$, pH, O$<em>2$, P, C, T; No; $t</em>{63}$=5 min</td>
<td>1 min; No; No*</td>
<td>Yes; 0.05 W for entire system</td>
<td>100 %, sensors affected by fouling at the end</td>
</tr>
<tr>
<td>PSI CO$_2$-Pro$^{TM}$ CV; NDIR</td>
<td>pCO$<em>2$; Yes 0 value; $t</em>{63}$=6 min</td>
<td>30 min; Yes; Yes TBT</td>
<td>No; 5-8 W</td>
<td>100 %</td>
</tr>
<tr>
<td>PSI CO$_2$-Pro$^{TM}$, NDIR</td>
<td>pCO$<em>2$; Yes 0 value; $t</em>{63}$=6 min</td>
<td>60 min; Yes; Yes TBT</td>
<td>No; 5-10 W</td>
<td>27 %, power cuts created overwriting of old data</td>
</tr>
<tr>
<td>Franatech CO$_2$; Solid-state electrolyte cell</td>
<td>pCO$<em>2$; No; $t</em>{63}$=No Data</td>
<td>1 sec; No; No</td>
<td>No; 7 W</td>
<td>50 %, data missing due to power cuts, noisy</td>
</tr>
<tr>
<td>University of Kyushu; ISFET</td>
<td>$2^*$pCO$<em>2$; No; $t</em>{63}$=No Data</td>
<td>30 sec; No; No</td>
<td>No; 0.02 W</td>
<td>75 &amp; 100 %, affected by fouling at the end</td>
</tr>
</tbody>
</table>

* Cu tape normally used in other deployments for antifouling protection

Figure 2. The FixO$^{3}$ node with the sensors after assembling.
Figure 3. Overview of pCO₂ data recorded with CONTROS HydroC™.

Figure 4. 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.
2.2 Field data correction of pCO\textsubscript{2} optodes

pCO\textsubscript{2} optodes from Aanderaa have been used in a wide range of applications from shallow water lake, coastal and aquaculture measurements to deep water deployments on fixed or moving (gliders) platforms. The main advantages of these sensors include good long term stability once they have been deployed, compact size and low power consumption, 6000 m pressure rated and low pressure hysteresis. The main disadvantages are the difficulty to get them well calibrated, relatively slow response time and unknown stability over longer deployment period than 12 months. Before start using these sensors there are limitations that the end user need to be aware of including:

They cannot be used in environments where there is H\textsubscript{2}S which is normally found in anoxic (no O\textsubscript{2}) environments. H\textsubscript{2}S will irreversibly contaminate the sensor foils.

The sensor cannot be allowed to dry out. A cap with water in it will have to be placed on the sensor whenever it is in air. The sensor has slow response (5 min) and has to be used with caution in profiling applications.

To obtain high accuracy data the end user will have to take high quality water samples for field adjustment sometime during the deployment. Preferably use DIC and Alkalinity to calculate pCO\textsubscript{2}. It is recommended to always measure O\textsubscript{2} (with optode) in parallel, this give quality control and a better understanding of the ongoing processes. As can be seen from the calibration figure below (example from Atamanchuk et al., 2014) pCO\textsubscript{2} optodes, just like other optodes, does not have a linear response with respect to solute concentration and temperature. For field correction, if a multipoint calibration has been performed, the whole calibration plane can however be moved up or down using just one reference point.

![Figure 5: Typical multipoint calibration curve for pCO\textsubscript{2} optode from Atamanchuk et al. (2014). For field adjustments the whole plane can be moved up or down using just one/some reference points.](image)

One simple and approximate field method for single point referencing of a pCO$_2$ sensor before and after deployment is to place the sensors in constantly air-bubbled water, e.g. with aquarium pump, with approximately the same salinity as at the deployment site. This should be done in an environment that is open to the atmosphere. Doing this inside a laboratory should be avoided since there could be large changes in CO$_2$ depending on the number of people and activities in the room. As a reference for the concentration in the bubbled water the atmospheric concentration (normally around 400 µatm), which is specific for the region and season, can be used.

The recommended steps of sensor handling to obtain higher quality long-term field measurements are the following:

1. After calibration put the sensor in water that has similar salinity (±5 psu) as the water in which it will be deployed.
2. Keep the sensor wet at all times until it is submerged. For longer storage the black cap + sponge delivered with the sensor can be used. Tape around the lower edges of the cap to prevent water from escaping. To keep the sensor wet also just before deployment place toilet paper soaked in seawater of the right salinity on the foil. This paper will dissolve and be washed away when the sensor enters the water.
3. Let the sensor acclimatise (possible osmotic effects) for at least three days before taking reference water samples for adjustment. If possible deploy O$_2$ optode and Salinity sensor close to the pCO$_2$ optode. The normal reverse correlation between O$_2$ and pCO$_2$ will give additional quality control and the possibilities to study on-going processes.
4. If possible take reference water samples in the proximity of the sensors during at least two occasions during the deployment to be analysed for DIC and Alkalinity and calculate pCO$_2$ (with CO$_2$sys).
5. Use CO$_2$ optode specific Excel sheet, provided with the sensor, that contains the equations to convert sensor raw data (Cal Phase) to pCO$_2$ values taking into account the sensors specific calibration coefficients. Please verify that the coefficients in the sensor and in sheet are the same. The coefficients are available by connecting the sensor to a PC (see manual).
6. Use adjustment coefficient in the Excel sheet to tune first set of reference data to sensor readings.
7. Verify with reference readings at other occasions that the sensor has been stable during the entire deployment.
8. If it is of interest to study and better understand the on-going processes in the studied area pCO$_2$ should be combined with another parameter in the carbonate system (preferably Alkalinity) to obtain DIC (calculated using CO$_2$sys).
9. Changes in molar ratios between DIC and Oxygen can be compared and used to quantify and understand the on-going processes. For more information about how this can be done see Atamanchuk et al. (2015) Continuous long-term observations of the carbonate system dynamics in the water column of a temperate fjord. *Journal of Marine Systems* **148**, 272–284.
The step-by-step procedure described above is targeted for pCO₂ optodes. Several of these steps should also be applicable to other pCO₂ technologies including: Take reference water samples at least two times during a deployment; Measure O₂ and Salinity in parallel with pCO₂; Establish relation between Salinity and Alkalinity to be able to use measured Salinity as a proxy for Alkalinity. Then use Alkalinity + pCO₂ to calculate DIC; Use changes in molar ratios of DIC and Oxygen to quantify and understand the on-going processes.

2.3 On-going TNA at E2-M3A

The on-going TNA COMBO (Fig. 2) combined clear water testing of new acoustic profiling instrumentation with high frequency optode measurements of pCO₂ and pH in surface and deep waters at E2-M3A) has been successful in improving Oxygen and Conductivity/Salinity data quality from one of the deep-water multi-parameter instruments. Field methods to check and improve data quality during service expeditions have been tested and implemented. Valuable information has also been collected on the performance of a new low power acoustic Doppler Current Profiling Sensor (Broad Band). Results from shallow water placed pH, pCO₂, Cond/Sal/Temp and Wave/Tide sensors are expected after recovery of this equipment during the first months of 2017.

At the same buoy two other instruments are mounted for long-term measurements of pCO₂ (NDIR technology from PSI, Canada) and one pH (from Sunburst, USA).

Figure 6: Buoy with SeaGuardII instrument for TNA COMBO is being deployed in the Adriatic Sea in April 2015.
2.4 Low energy logger/communication hub and sensors on autonomous Sailbuoy

In a Norwegian project called Iceedge an autonomous Sailbuoy (Offshore sensing, Bergen, Norway) was equipped with a stand-alone logging/transmission/sensor package from Aanderaa Data Instruments (Bergen, Norway) and sent off for a mission along the ice edge in the Arctic (Fig. 7).

![Sailbuoy](http://cmr.no/projects/10385/sailbuoy/)

Figure 7: Standalone package on Sailbuoy consists of Logger, GPS, Iridium modem, UV light for antifouling and sensors for Sal, Temp, 2*O₂ (one in air the other in water), pCO₂ and pH.

Data from all sensors seems was of high quality (Fig. 8). There is a clear expected anti-correlation between O2 (287-347 μM, salinity compensated, decreasing) and pCO₂ (365-560 μatm, increasing) as well as between pCO₂ and pH (7.7-7.8, increasing).

pH has a stabilisation time of about 1 day in the beginning. Reference data were collected and will be used to adjust absolute values of pH and pCO₂ and to determine if there was drift.

All 4 temperature sensors (4.9-9.0 degC, increasing) in the water give the same readings within 0.01 degC. The temp sensor (on 4330 O₂ optode) on top of the hull is in the atmosphere and exposed to the sun and shows higher average temperature and higher variations (3.0-17.3 degC). Salinity varies between 34.5-35.1.

Oxygen optodes show no sign of drift (close to 100 % in air at start and end). Oxygen is mostly oversaturated (primary production) in the surface water. Comparing with atmospheric readings and taking into account wind speed will give possibility to calculate export/import of O₂ to/from the water/atmosphere. The resolution of the pCO₂ optode is better than 2 μatm and of the pH optode better than 0.005 units.
3. CONCLUSIONS

1. In the Best Practice Handbook methods are suggested to enhance the capability of the FixO³ infrastructures for high quality observations. Above a specific example is given for field improvements of pCO₂ optodes/sensors.

2. In FixO³ we have field evaluated pCO₂ and pH sensing technology from the aspect of performance, size and energy consumption. Examples of well performing, low energy consuming, multipara meter platforms with large expansion possibilities are given in this report. An interfacing exercise is planned under task 4 of this WP12.

3. The additional knowledge gained thanks to TNA experiments inside FixO³ will be analysed after the end of these TNA during the first half of 2017. This will allow a conclusion on the long term deployment issue. It will be further reported in the final report in complementarity with this deliverable.