Project Information

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Deliverable information

Deliverable information	
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Description	**Implementation of pH sensor on Eulerian observations in the Mediterranean Sea (DYFAMED site)**
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Lead beneficiary	SU
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Comments	Due to the delay of sensor shipment (1.5 year), the deliverable focuses on the sensor quality check and the deployment procedure. The manufacturer (SeaBird) experienced delays in the delivery of essential parts for the manufacture of the sensor.

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Executive summary

The ability of fixed platforms to accurately measure CO2 variables in a changing ocean is critical today. Thanks to technological advances we can now observe long-term pH variability. In this deliverable we have tested and validated the integration of a pH sensor (Seabird) adopted by the BGC-ARGO community on a site in the Ligurian Sea which benefits from a monthly sampling allowing to validate the quality of the data. The data obtained over 5 months have demonstrated the robustness of the sensor and the good accuracy compared to in situ measurements. We also estimated a slight offset comparable to other measurements with this type of sensor, offset easily adjustable with the reference in situ measurements. This type of observation will continue in the future and will improve our observations of CO2 in the Ligurian Sea.

1.   Introduction

Ocean pH is a dynamic variable that changes on daily, seasonal, interannual, and decadal to centennial time scales. Variability on daily to annual time scales is produced by a variety of processes, including photosynthesis, respiration, heating, and ocean physics. The short-term changes are superimposed on a century-scale decrease in surface ocean pH, at a rate near -0.002 pH per year, which is due to the long-term increase in atmospheric carbon dioxide created by fossil fuel burning. This long-term decrease in pH, called ocean acidification, can have profound effects on some organisms. Observations of pH changes on annual or weekly scales provide important constraints on net photosynthesis and respiration in the ocean.

The Mediterranean Sea is a very dynamic regional sea. Because of its semi-enclosed nature and low inertia, due to the relatively short residence time of its water masses, it is highly reactive to external forcing variables, in particular to variations in water, energy and matter fluxes at the interfaces (Durrieu de Madron et al., 2011). The role of the Mediterranean Sea as a source or sink of atmospheric CO2 in the global carbon cycle, especially in the context of warming Mediterranean Sea waters, is unclear (Nykjaer,2009; Vargas-Yanezetal.,2008). Several recent studies indicate a gradual shift from source to sink over the last decades (Louanchi et al., 2009; Taillandier et al., 2012). However, in situ measurements of the seawater carbonate system are still rare for the Mediterranean (Coppola et al., 2020). In recent years, a few cruises have provided a clearer description of the carbonate system at the basin scale (Alvarez et al., 2014). For the northwestern region, time series of carbonate chemistry exist in the Ligurian Sea at DYFAMED and ANTARES (Merlivat et al, 2018; Touratier and Goyet, 2009), in the Bay of Villefranche-sur-Mer at the Point B station (Kapsenberg et al., 2017), and in the Gulf of Trieste in the coastal water (Ingrosso et al., 2016). However, these measurements are very spotty and do not allow us to understand the seasonal and interannual surface variability of the pCO2-pH

In recent years, technological advances have allowed the deployment of robust and quality pH sensors at sea (Miller et al., 2018). Combined with pCO2 measurements, these fixed-point measurements at the surface would allow a better estimation and understanding of the evolution of CO2 fluxes at the air-sea interface. For this, the DYFAMED site already has high frequency pCO2 measurements at the surface since 2013 (Merlivat et al., 2018) and the installation of a new pH sensor (already tested and acquired by the Argo community) would improve our CO2 observations in the Ligurian Sea.

2.   The choice of the sensor: SEAPHOX (Seabird)

Honeywell's Durafet is an ion-sensitive field-effect transistor pH sensor (*Figure 1*). It has been shown to have exceptional stability and accuracy. The conduction channel of the transistor is coated with an insulator whose surface is covered with an amphoteric oxide. The surface charge of this coating depends on the pH of the solution. Changes in the pH of the solution then alter the potential of the conduction channel and the performance of the transistor, allowing the pH of the ocean to be measured. For our project, we chose a shallow SEAPHOX that combines both T, S, O2 and pH measurements, essential variables to recalculate the carbonate system variables.

SeapHOx V2 combines the SeaFET V2 SEAFET pH sensor with the SBE 37-SMP-ODO MicroCAT CTD+DO sensor. The SeapHOx V2 allows for the integrated data collection of pH with the critical oceanographic and biological measurements of temperature, salinity, and oxygen. The integrated package also allows the SeaFET V2 to take advantage of the SBE 37's pumped flow path and anti-fouling technology, ensuring long-term stability and extending deployment duration.
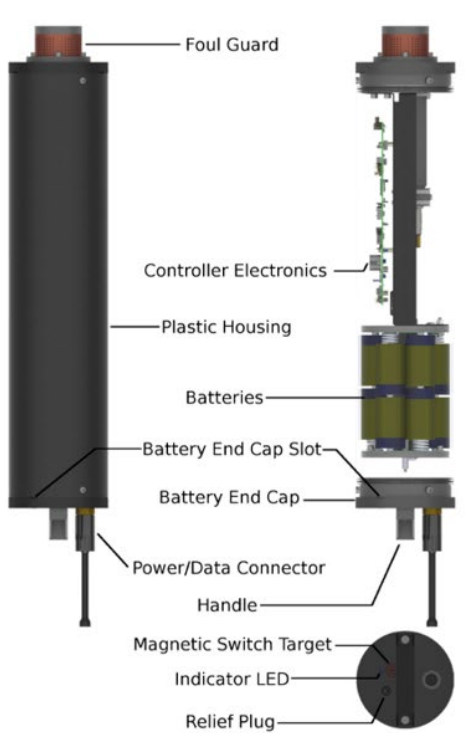

Figure 1. Left: Description of the Ion Selective Field Effect Transistor (SEAFET) pH sensor (picture from Seabird). Right: SEAPHOX v2 sensor in the LOV lab (CTDO2 + SEAFET)

3.   Deployment procedures

The external reference pH electrode requires several days to condition to the seawater at the deployment site before providing optimal data. If possible, it is recommended by the manufacturer to store the pH sensor (SEAFET) in filtered seawater at the deployment site prior to deployment to reduce conditioning time.

To do this, we conducted a 2 weeks test in September in a tank installed in the laboratory. The tank was filled with seawater pumped from the bay and filtered to avoid fouling by phytoplankton.

This test follows these procedures:

Step 1: deployment of the sensor in a tank for 2 weeks to allow the SEAFET (pH sensor) to stabilize when it is new. We deployed the sensor facing up and expel the air from the SEAFET cap at launch to avoid air bubbles at the various sensors. The SBE 37's pump is not strong enough to expel them when the sensor is started. During the measurement the SBE37 pump starts 38s before the SEAFET (*Figure 2*)

Step 2: after these 2 weeks, the sensor made one measurement per hour at a fixed time and we sampled the seawater of the tank near the sensor at the same acquisition times to measure pH by spectrophotometry and dissolved oxygen by Winkler method once a day for one week

Step 3: Once the data were validated, we proceeded to deploy the sensor on the BOUSSOLE buoy at 3 m depth near the CARIOCA pCO2 sensor already installed since 2013 (Merlivat et al., 2018). To limit the biofouling effect, we have mounted a cupper cap on the top of the pH sensor (*Figure 2*)
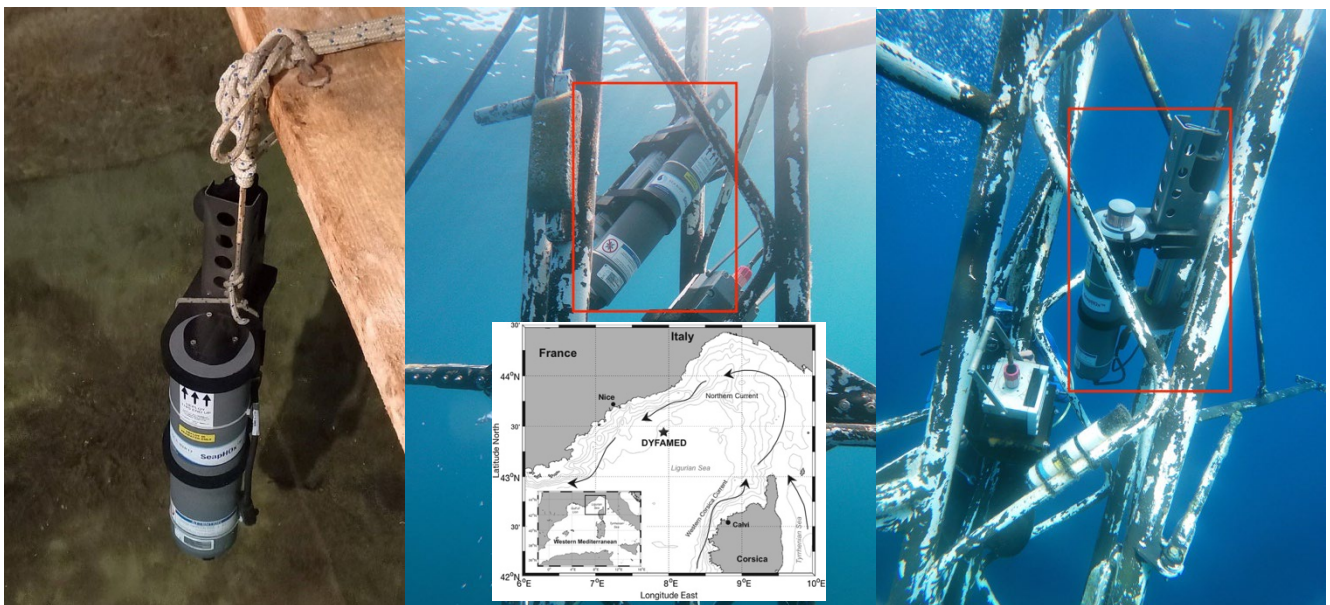

Figure 2. Left: Deployment of the SEAPHOX sensor in the Villefranche tank. Right: Installation of the sensor at the DYFAMED site (Boussole buoy) at 3m depth near the pCO2 CARIOCA sensor

4.   Quality control procedures

The sensor data acquired during the lab test have been compared to in situ measurements for oxygen and pH (*Figure 3*). During the deployment, we observed a short shutdown of the tank pump that caused a decrease in S and pH and an increase in oxygen due to bubbles caused by the restart of the tank pump.

After two weeks of deployment, the SEAFET sensor was stabilized. The DO data show some offset (around 10-15 µmol/kg) due probably to a non-adapted method for Winkler sampling (presence of bubbles in the vial). In addition, the range of offset is typical for optode sensor even after recent calibration (Bittig et al/,

2018). On the other hand, the pH samples (less sensitive to the bubbles) show a good consistency with the pH sensor (*Figure 3*).
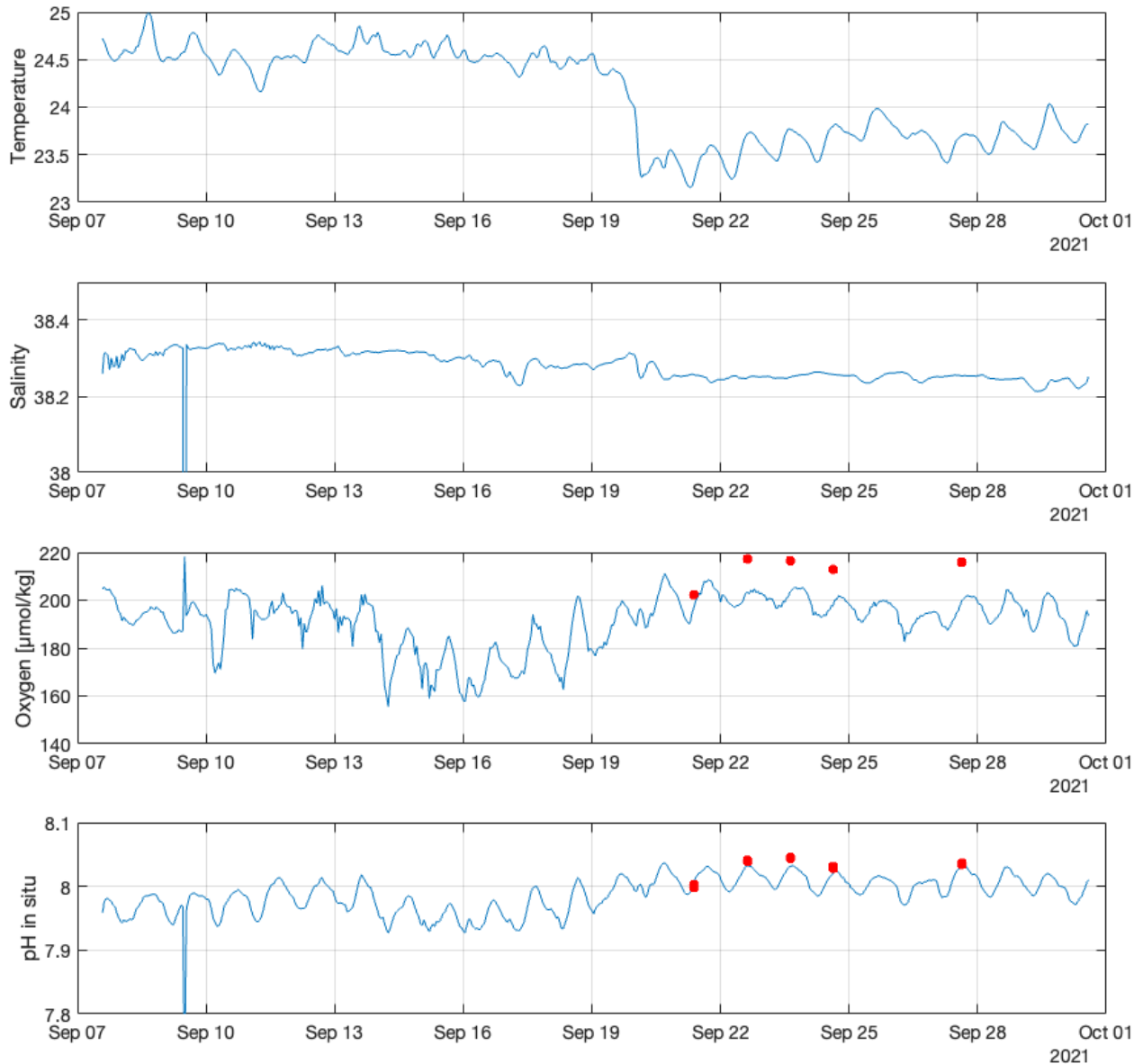

Figure 3. First SEAPHOX dataset acquired from 07 September to 01 October inside the tank before the sensor deployment. The red dots for DO and pH represent the in-situ sampling

5.   Validation at sea

The SEAPHOX sensor was deployed at sea from 13/10/2021 to 7/03/2022 at 3m depth at the DYFAMED site (BOUSSOLE buoy). The sensor measured P, T, S, O2, and pH hourly and the data were compared with monthly MOOSE cruises that provided in situ DO and pH values at the same depth. Samples were analysed in the LOV laboratory using Winkler and spectrophotometric techniques.

The *Figure 4* presents the SEAPHOX data variability and comparison with in situ analysis from 13/10/2021 to 07/03/2022.
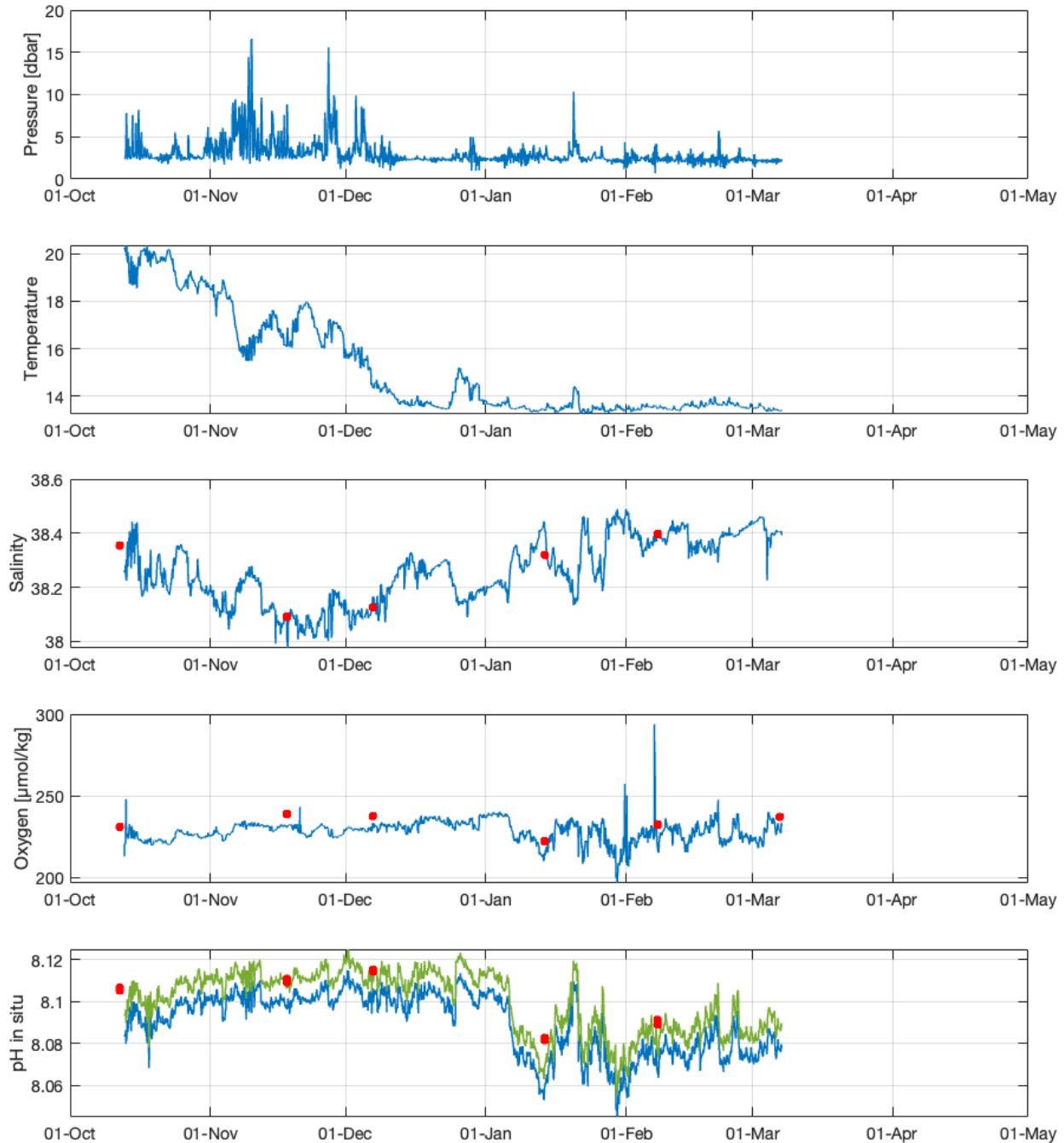

Figure 4. Hourly data provided by the new SeaPHOX sensor deployed from October 13th to March 7th at the DYFAMED site (3m depth). The red dots correspond to the monthly in situ sampling (salinity, oxygen and pH). For the pH panel, the green plot represents the adjusted pH values

During the winter period 2021-2022, the SST decreased rapidly from 20°C to 13.5°C while the SSS decreased from October to early December (38.4 to 38) and increased to reach again 38.4 in early February. The SSS

variability is typical from previous observations in the Ligurian Sea (Coppola et al., 2018). The SSS depends on the balance between evaporation and precipitation rate and the winter mixing that mixes the Atlantic waters with the saltier intermediate waters. During the same period, the DO concentrations ranged from 200 to 290 µmol/kg with higher concentrations near surface which is consistent with seawater cooling and the increase of oxygen solubility.

Finally, the SEAPHOX values showed an offset of 0.01 pH units during the deployment period. To adjust the pH values, we used the SeaCarb 3.3.0 toolbox (Gattuso J.P. et al. 2021) to estimate new calibration coefficients for the SeaFet pH sensor (E0INT,25, E0EXT,25). The new adjusted pH values are then obtained after post-processing of the data using the new SEAFET coefficients (green line in *Figure 4*).

Thus, we observe that during the deployment period, the adjusted pH values vary from 8.05 to 8.12 pH units. These are consistent with the pH variability observed from 1995 to 2011 at DYFAMED in surface waters (Yao et al., 2016): pH increases from late fall to early winter and then decreases rapidly in January when SSS is higher before increasing from February. The variability of pH is expected to be related to the flux of pCO2 into surface waters, but at this time pCO2 data from the CARIOCA sensor have not been collected.

6.   Conclusions and perspectives

We have seen in this report that the SEAPHOX sensor deployed on the surface at DYFAMED is a critical sensor for accurately measuring pH variability. Through laboratory testing prior to sensor deployment and monthly visits to the DYFAMED site, we were able to demonstrate the proper functioning of the pH sensor. Even if the deployment period discussed here is short (5 months) and does not allow us to estimate the possible risks of drift of the sensor, the first values obtained are promising for the continuation of the project.

For the rest of the project, the SEAPHOX sensor will still be deployed on the surface at the DYFAMED site and will be supported by pCO2 measurements from the CARIOCA installed since 2013 at the DYFAMED site. This pair of pH-pCO2 sensors associated with monthly ship measurements (AT-CT-pH) will thus offer a good approach to improve our observations of the carbonate system in the Ligurian Sea. Associated with the CANYON-MED neural network used to predict the AT-CT-pH values (Fourrier et al., 2020), these observations will be essential for the elaboration of the carbon audit planned in task 7.1 of the EUROSEA project.

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