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ENVRI^plus DELIVERABLE

# D1.3
# Final prototype of Argo float with pCO2 and pH launched

## WORK PACKAGE 1 – New Sensor technologies: innovation and services

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ABSTRACT

pCO2 concentration in the ocean water is of a main importance for the comprehension of the Carbon cycle, and in particular to assess the rate of Ocean acidification and its evolution in the time and space.

Global measurements of physical, chemical and bio-geochemical parameters over the entire ocean are ensured by the Argo program, using a network of about 4000 profiling floats, which technology evolved progressively over years to be able to carry additional sensors.

This document presents the developments to integrate a pCO2 sensor on a profiling float, with the associated cave outs and successes.

The scientific assessment of the data collected at the end of the project will be pursued and published as a follow-up to this document.

Project internal reviewer(s):

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# DOCUMENT AMENDMENT PROCEDURE

Amendments, comments and suggestions should be sent to the author

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# TERMINOLOGY

A complete project glossary is provided online here: https://envriplus.manageprojects.com/s/text-documents/LFCMXHHCwS5hh

# PROJECT SUMMARY

ENVRIplus is a Horizon 2020 project bringing together Environmental and Earth System Research Infrastructures, projects and networks together with technical specialist partners to create a more coherent, interdisciplinary and interoperable cluster of Environmental Research Infrastructures across Europe. It is driven by three overarching goals: 1) promoting cross-fertilization between infrastructures, 2) implementing innovative concepts and devices across RIs, and 3) facilitating research and innovation in the field of environment for an increasing number of users outside the RIs.

ENVRIplus aligns its activities to a core strategic plan where sharing multi-disciplinary expertise will be most effective. The project aims to improve Earth observation monitoring systems and strategies, including actions to improve harmonization and innovation, and generate common solutions to many shared information technology and data related challenges. It also seeks to harmonize policies for access and provide strategies for knowledge transfer amongst RIs. ENVRIplus develops guidelines to enhance transdisciplinary use of data and data-products supported by applied use-cases involving RIs from different domains. The project coordinates actions to improve communication and cooperation, addressing Environmental RIs at all levels, from management to end-users, implementing RI-staff exchange programs, generating material for RI personnel, and proposing common strategic developments and actions for enhancing services to users and evaluating the socio-economic impacts.

ENVRIplus is expected to facilitate structuration and improve quality of services offered both within single RIs and at the pan-RI level. It promotes efficient and multi-disciplinary research offering new opportunities to users, new tools to RI managers and new communication strategies for environmental RI communities. The resulting solutions, services and other project outcomes are made available to all environmental RI initiatives, thus contributing to the development of a coherent European RI ecosystem.

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# 1 RATIONALES

## 1.1 the necessity to measure pCO2 in oceans (ocean acidification, cycle of the carbon, ...)

The ocean absorbs about 25 % of anthropogenic carbon dioxide ($CO_2$) emissions (Le Quéré et al., 2016), moderating the rate and severity of climate change. Such massive input of $CO_2$ generates sweeping changes in the chemistry of the carbon system, including an increase in dissolved inorganic carbon ($C_T$) and bicarbonates ($HCO_3^-$) as well as a decrease in pH and in the concentration of carbonate ($CO_3^{2-}$) ions. These changes are collectively referred to as "ocean acidification". The pH of ocean surface water has decreased by 0.1 units since the beginning of the industrial era, corresponding to a 26 % increase in hydrogen ion concentration, and the total decrease by 2100 will range from 0.14 to 0.4 units (Gattuso et al., 2015). These changes are, however, quite variable regionally and with depth (Orr et al., 2005). Elucidating the biological, ecological, biogeochemical and societal consequences of ocean acidification therefore requires a fine resolution of ocean $CO_2$ data in space and time. Thus, humankind is in urgent need of routine and sustained global information on the marine environment sufficient to meet society's needs for describing, understanding and forecasting variability and long-term change. We do know, however, that significant marine CO2 sources and sinks exist in currently under sampled or even unsampled areas (Bakker et al., 2016; Takahashi et al., 2009), which are undergoing rapid anthropogenically driven change and exhibit high vulnerability (e.g., increasingly ice-free Arctic Ocean, Southern Ocean, coastal seas).

## 1.2 the specifications (sensitivity, accuracy, ...) for an optimal pCO2 sensor for autonomous platforms ensuring the continuity with surface

Still, pCO2 sensors that can be mounted on autonomous measurement platforms have lower accuracy than the bulky installations one can install on research vessels or commercial ships. However, these sensors having a lower accuracy (up to +- 5µatm) but being deployed in higher numbers can increase our understanding of vast areas of the global ocean. A comprehensive description of the needed specifications of these sensors is given in Wanninkhof et al. (2013). Fig. 1 shows data from an autonomous sensor installed on a drifter buoy for a 24-hour drift experiment. The drifter was deployed in a oligotrophic region of the Indian Ocean but a diurnal cycle of 2 µatm could be resolved with the sensor. These results show the capability of modern sensors. It needs to be noted that the shown results were recorded in a slowly changing environment and response times didn't play a major role.

## 1.3 Resume

In the past decade the ocean carbon cycle community made huge progress in making diverse datasets available in a streamlined manner. This enabled new insights in the global carbon cycle (e.g. Rödenbeck et al., 2015) and showed the potential of big datasets. However, most datasets were recorded with classical methods which ensure highest accuracy of the single data points but might lack of temporal and special information. By outfitting autonomous devices (as gliders, floats,…) with sensors based on new technologies (membrane based gas sensors, optodes,…) one can overcome the temporal and spatial downfall by compromising a little bit in terms of accuracy.

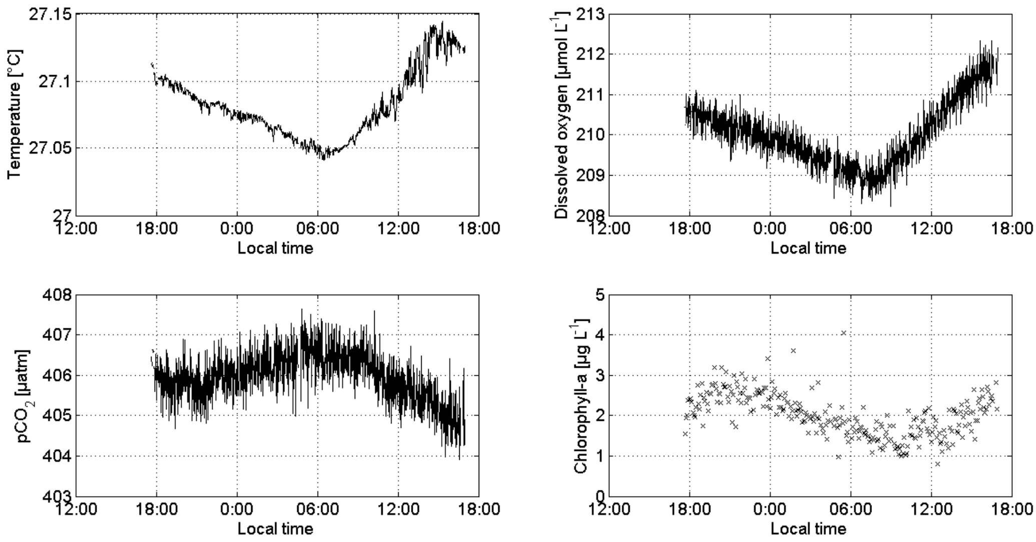



*Figure 1. Data from a drifter experiment: Temperature sensor (Seabird SBE37), oxygen sensor (Aanderaa optode 3880), Chlorophyll sensor (Wetlabs FLNTUR) and pCO2 sensor (KM Contros HydroC CO2) were installed at approximately 10m depth. They were attached to surface drifting buoy.*
*The figure shows non-published data (T. Steinhoff, GEOMAR) from a cruise to the Indian Ocean.*

## 2 Review of available technologies/sensors at the ENVRIplus Start

At the beginning of the ENVRIplus project in May 2015, only few commercially available sensors where suitable for implementation on the Argo network platforms.

Autonomous platforms such a profiling floats requires extremely mature components as the probes are operating in the open ocean without any human intervention during their entire lifetime.

The requested Technical Readiness Level (TRL – EC classification) for the candidate sensors cannot be less than 8 ( system complete and qualified) or even better 9 (Actual system proven in operational environment), due to the constraints of the ambient environment- High pressure (200 bars and more), corrosion (saline waters), and to the technical challenges – Size and volume as small as possible, extremely low energy consumption to ensure the compliance with the four years at sea lifespan of the global Argo network material.

In 2014 and 2015, The FixO3 FP7 Project performed a review of existing pCO2 sensors and a field inter-comparison campaign, resulting in a study on which ENVRIplus can draw on for its own purposes. FixO3 network is composed of anchored moorings, and does not have such strong requirements in term of energy, sizing, autonomy as for autonomous platforms. One may thus benefit from the published deliverables **(REF)** to extract useful information summarized in the table below, describing the characteristics of explored pCO2 sensors:

| Instrument | Time response | Depth rating (m) | Weight in water (kg) | Current draw (A) without pump | Pumped | Commercially available |
|---|---|---|---|---|---|---|
| CONTROS HydroC | $\tau_{63}$ : 6min at 20°C unpumped<br>$\tau_{63}$: 90 sec pumped | 6000 | 2.2 | 0.3 | No/Yes | yes |
| Aanderaa 4797 | $\tau_{63}$ : 4 min | 6000 | < 0.1 | 0.004 | No | yes |
| PSI CO2-Pro | $\tau_{63}$ : 4 min | 200 | 0.4 | 0.45 to 1 | Yes | yes |
| PSI CO2-PRO CV | $\tau_{63}$ : 2.5 min | 4000 | 0.5 | 0.25 to 0.85 | Yes | yes |
| Franatech CO2 | $\tau_{90}$ : 20 min | 40 | 0.5 | 0.5 | No | yes |
| ISFET pCO2 | $\tau_{90}$ : <60 sec. | 6000 | 1.4 | 0.002 to 0.009 | No | No |

*Table 1. Summary of the characteristics of available sensors for pCO2 measurement in sea-water at the start of ENVRIplus project*

# 3 Choice of the most appropriate material

## 3.1 Criteria

The selection of the appropriate sensor for a mounting on a profiling float was driven by several considerations:

1. The complete system has to be compliant with the overall specifications of the Argo Network. The float should remain be able to sample continuously during its ascending profile and to transmit its data in real-time to the Data acquisition centers, the powering and sampling strategy is controlled by the float technical board, a lifespan of the complete system is maintained at four years or at minimum 150 cycles, the complete system is able to reach a depth of 2000 m.
2. The integration of the new sensors does not require strong hardware modifications on the float (physical integration, software)
3. The sensor does not require any human intervention after deployment, and its drift if occurring (ageing, biofouling, mechanical issues, calibration) can be monitored and/or corrected during data post-processing.

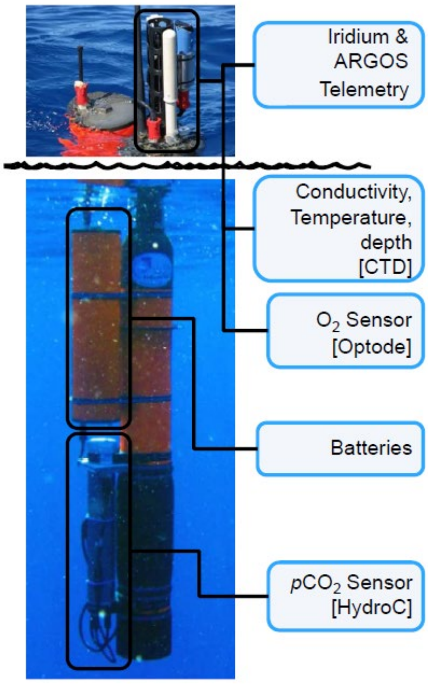
Considering the characteristics of the available sensors and the profiling floats requirements, only few of the material could be considered for the building of the prototype within the ENVRIplus project.

The pumped sensors have been eliminated for their high power consumption, sensors with insufficient depth rating (not less than 2000 m) as well, and for a sustainability reason prototype /demonstrator sensors where not retained.

Thus ISFET, Franatech and PSI material have not been selected, and focus has been pointed towards CONTROS and Aanderaa products.

## 3.2 Previous attempts to implement pCO2 on a profiling float

A first attempt to implement a PCO2 sensor on a profiling float has been performed by Fiedler et al. in 2010. A NEMO platform (Navigating European Marine Observer profiling float / Optimare GmbH, Bremerhaven, Germany) has been modified to be able to carry a CONTROS HydroC sensor, with its own battery pack and standalone water pump. The prototype deployed during a field campaign offshore Cape Verde Islands showed promising performances in term of pCO2 measurement ability, but its size, weight and energy balance due to the use of a highly consuming pump is not appropriate for Argo network long term deployment. This first prototype was designed to be recovered at sea after a mean period of about 40 days for hardware maintenance and data post-processing purposes.

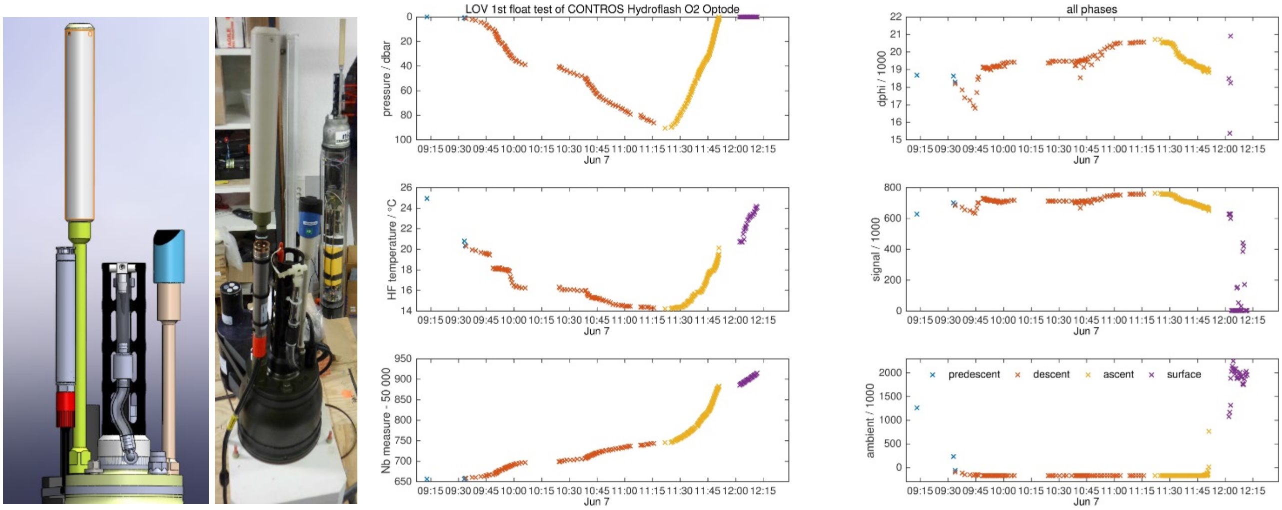



*Picture 1. First profiling float (NEMO model) equipped with a standalone KM CONTROS HydroC sensor and its battery pack – GEOMAR and KM CONTROS collaboration - 2010*

In collaboration with the Laboratoire d'Océanographie de Villefranche-sur-Mer (LOV), a proof-of-concept float (PROVOR) implementation of a CONTROS HydroFlash® $O_2$ optode was successfully achieved (see Fig. 2.A and 2.B). This step was necessary as a precursor for planned field work on $pCO_2$ optodes from CONTROS at that time, as those were meant to be based on the same instrument type. Therefore, the CONTROS HydroFlash® $O_2$ optode was entirely integrated in the top structure, power supply and data string transmission of the float besides the other sensors, namely a CTD and Aanderaa optode.

This dual-oxygen float was then deployed in the morning of 7$^{th}$ June 2016 in the Mediterranean Sea off the coast of Villefranche-sur-Mer. This test profile can be seen in Fig. 20.C, where data is shown for pressure (dbar, from CTD) as well as temperature (°C), number of measurements, phase shift (°), signal intensity (mV) and ambient light (mV; all from HydroFlash® $O_2$ optode). Generally, data points are shown for 4 different phases of the floats cycle, i.e. pre-descent, descent, ascent and surfacing. While all measurements show normal behavior before the float's full ascent, the optode revealed a strong cross-sensitivity of the sensor spot when exposed to direct solar irradiation at the surface at about 12:00 pm.

Overall, the collaboration with the LOV and results from the test gained important information for both GEOMAR scientists and CONTROS developers. This test revealed an issue with the sun-shading of HydroFlash® $O_2$ optode, while for the rest of the profiles data was successfully recorded without peculiarities. Further tests could not be carried out.

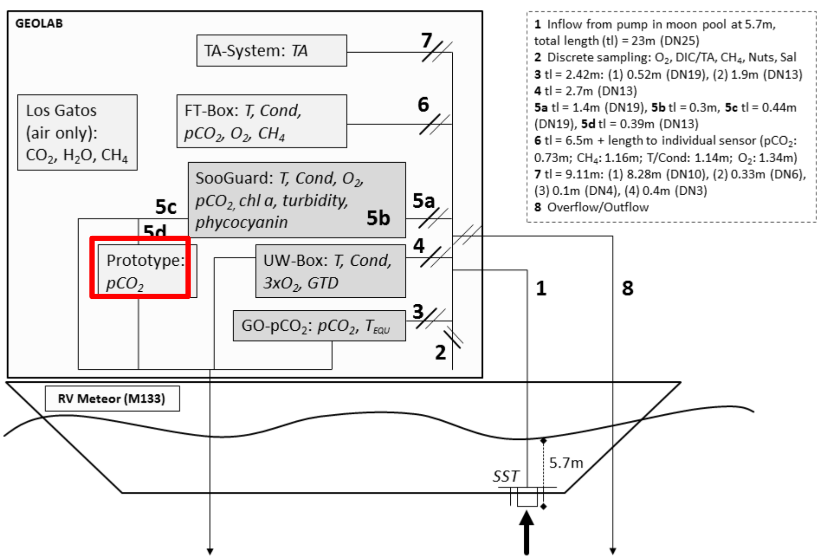



**(A)** **(B)** **(C)**

*Figure 2: (A) Schematic arrangement of the CONTROS HydroFlash® $O_2$ optode next to the CTD and Aanderaa optode on a PROVOR float. (B) Successful proof-of-concept float (PROVOR) implementation of a CONTROS HydroFlash® $O_2$ optode as a precursor for further work on $pCO_2$ optodes. (B) First profile of the CONTROS HydroFlash® $O_2$ optode recorded during the test deployment (Drawing and figures kindly provided by Christoph Penkerc'h/LOV and Henry C. Bittig/LOV).*

A first prototype of a planar $pCO_2$ mini sensor spot optode (SN DCO2-1116-001) provided by CONTROS, was initially tested in the course of a research cruise (R/V Meteor cruise M133) across the South Atlantic (15.12.2016 – 13.1.2017). The spot optode was integrated in a custom-made flow-through chamber with simultaneous temperature recording. Fig. 21.A schematically shows all underway measurements during M133 in which the $pCO_2$ prototype was integrated (flow line 5d, red box). Optical, continuous $pCO_2$ measurements with this prototype were carried out throughout the cruise using a measuring interval of 30 seconds. In total, data were recorded for 17 days. For comparison, an Aanderaa $pCO_2$ optode sensor (model 4797) was installed in the flow-through chamber SOOGuard. Part of the full setup is shown in Fig. 21.B. Further information is available in the M133 cruise report (provided on request).

**(A)**



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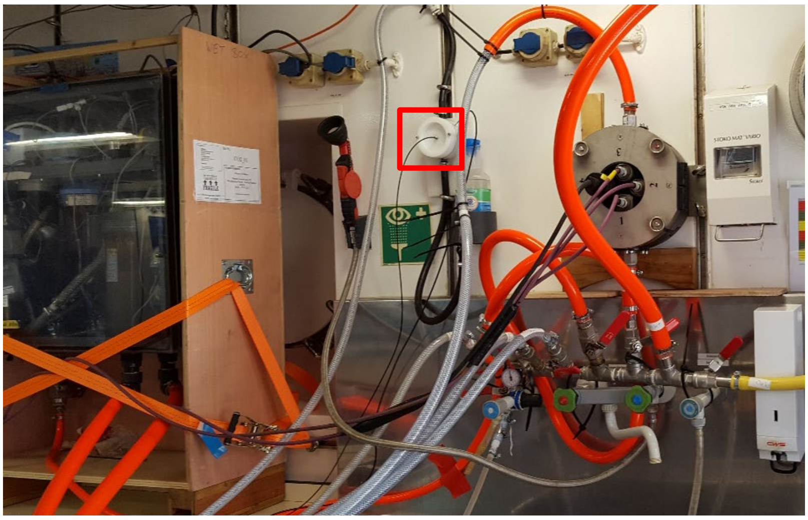


*Figure 3 : (A) Schematic overview of all underway measurements carried out during the research cruise M133 of R/V Meteor. The CONTROS pCO2 prototype (flow line 5d, red box) was arranged directly behind optical pCO2 measurements from an Aanderaa pCO2 optode (model 4797). (B) Arrangement of the pCO2-GO-system (left), CONTROS pCO2 prototype sitting in a flow-through chamber (middle, red box) and the SOOGuard system (right; picture and figure by Tobias Hahn/GEOMAR).*

The data acquired both from the Aanderaa $pCO_2$ optode sensor (see Fig. XX.A) as well as the CONTROS prototype of a planar $pCO_2$ mini sensor spot optode (not shown here) did not provide useful data as compared to the reference GO underway $pCO_2$ system (see Fig. XX.B). After a trans- Atlantic section along 34.5°S (departure from Cape Town/South Africa) with relative stable $pCO_2$ in the 370-410 µatm, a generally lower and more variable $pCO_2$ of 220-360 µatm was encountered on the Patagonian Shelf from Jan 4$^{th}$ onwards. The Aanderaa $pCO_2$ optode does detects $pCO_2$ features qualitatively, particularly towards the end of the cruise. However, the $pCO_2$ data show a (i) a rather long conditioning phase (> 2 days), (ii) very long response times that do not allow to resolve the $pCO_2$ variability in the open South Atlantic, and (iii) a large drift pattern towards higher $pCO_2$. The data acquired with this optode therefore do not meet minimum quality requirements even for underway work.

Similar observations have been made elsewhere and points at the not satisfactory level the optode technology has reached with respect to $pCO_2$.

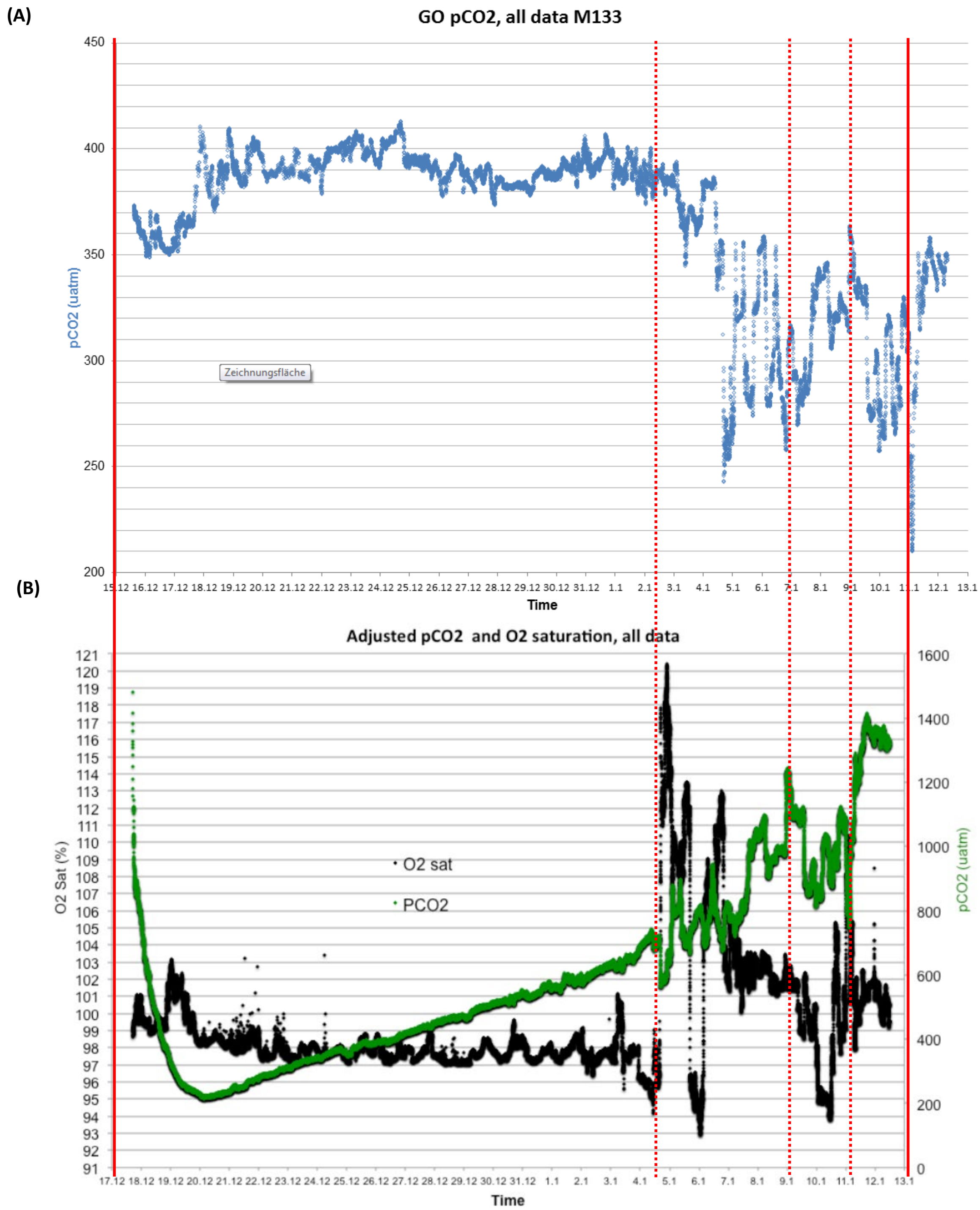



*Figure 4. Reference $pCO_2$ data from the GO underway $pCO_2$ system (A) and the Aanderaa $pCO_2$ optode (B, green symbols) as recorded between 15.12.2016 and 13.1.2017 over the course of the M133 cruise of R/V Meteor. After a trans-South Atlantic section along 34.5°S (departure from Cape Town/South Africa), data were recorded over the Patagonian Shelf from Jan $4^{th}$ onwards.*

Unfortunately, despite constant and promising developments performed by CONTROS Gmbh, Their acquisition by KONGSBERG company with new development strategy combined to a lack in the procurement of key internal components led to a pause, then an adjournment in the further developments of this sensor, new time schedule becoming incompatible with the ENVRIplus project Timeline.

### 3.3 Retained solution

It has been then decided in accordance with the Task's Partners to consider the last sensor available, the Aanderaa 4797 pCO2 Optode, in order to be able to fulfill the task's objective, and despite the known weaknesses of this sensor.


*Picture 2. Aanderaa/XYLEM pCO2 Optode ref 4797 selected for an implementation on the profiling float*

This sensor holds all the technical characteristics for compliance with an Argo float implementation:

1. Small in size and light in weight
2. Common physical and software interface as Aanderaa 4330 Oxygen optodes already stalled on profiling floats for years, easing the physical integration on platform's head
3. Low energy consumption
4. No maintenance required after deployment

The main weakness of this sensor consists in its slow time response ($\tau_{63}$) of about 4 to 5 minutes for a stabilized measurement, and its high sensitivity to Hydrogen sulfide (H2S) leading to an irreversible damage of the sensor's foil in case of exposure – risk in anoxic waters.

Another weakness of the sensor is that to maintain its calibration at the requested level, the sensor's foil has to be maintained wet during its complete lifetime (even during storage) and that it has to be soaked in a water with the same Temperature/Salinity characteristics as the deployment water for preconditioning the diffusive effects of the foil's components.

As no development of this commercially available sensor was scheduled to improve its weaknesses, a decision has been endorsed by IFREMER – the partner in charge with the prototype development – to work on the float's software side to adapt the profiling scheme of the platform to the sensor's characteristics.

The provided solution consisted in adding an additional controlling board in the float for the sensor piloting, and adapting the descending profiles to a "ladder scheme" allowing the float to stabilize itself in a stable water mass during the requested time for a suitable pCO2 measurement.

The profiling float (*NKE Instrumentations* Provor model) does not allow a retrofitting action from sensor to vector for the control of the position of the system in the water column, thus the piloting software of the float required also some improvements to implement the new descending profiling scheme.

The modification of the global sampling strategy of the float's software would have been too deep and incompatible with the standard behavior requested by the Argo network. As the final product was a prototype, the R&D team abandoned a parametric sampling strategy for pCO2 measurements, the functioning of the float allowing to automatically select key phases during the descending profile when the platform is intrinsically stabilized at a still pressure level.

The float controls its descending speed monitoring the pressure sensor measurements. Through its journey to depth, the floats is progressively slowed down due to the increase of the ambient density. When the float's speed undergoes a pre-defined level, the controller decreases the volume of the float by opening of a solenoid valve on the hydraulic system. Usually a slight change of the float's volume allows to pursue the descent without strong speed disruption. To allow a near to complete stop of the float for pCO2 measurements, the controller's software/hardware has been modified to enter a freeze mode before the solenoid valve action for a duration in line with the pCO2 sensor acquisition time (around 2 seconds). The sensor controlling board performs the powering on, measurements, powering off of the sensor, hand is given back to the float's controlling board which resumes with the buoyancy management allowing the float to pursue its descent.

The weakness of this sampling strategy resides in the fact that the ladder shaped descending profile cannot be set with fixed parameters (one measurement every X meter for example).
The data acquisition is fully controlled by the float's buoyancy, which fully depends on the ambient water density and on the buoyancy state of the float when it left the surface. As these two parameters are varying across the profiles, the resolution of pCO2 measurements cannot be fixed and will depend on the number/frequency of the solenoid valve actions required to move the float to its targeted drifting depth.

Measuring at descent is not a standard Argo feature. The majority of floats manufacturers including NKE Instrumentations have thus included this ability in their material. For NKE Instrumentations PROVOR float, measurements at descent are only enabled from surface to drifting depth. For pCO2 measurements purpose, the drifting depth of the float will be positioned at the same depth as the sampling one, departing from the standard Argo profile.

Additionally to at depth measurements, Surface sampling of pCO2 has been implemented at the end of the ascending profile both when float is positioned at sub-surface, and when fully emerged.

As a consequence of the new profiling scheme (see Figure 1), and knowing that a standard drifting period for Argo floats is 10 days, the pCO2 descending measurements representing the profiles will be collocated with CTD data form the previous cycle. At the contrary, the sub-surface and above surface measurements will be collocated with the actual cycle's CTD profile. This means that post-processing in Real Time will be implemented on data decoding chains on-shore to correctly position geographically the pCO2 data and accurately time stamp them.

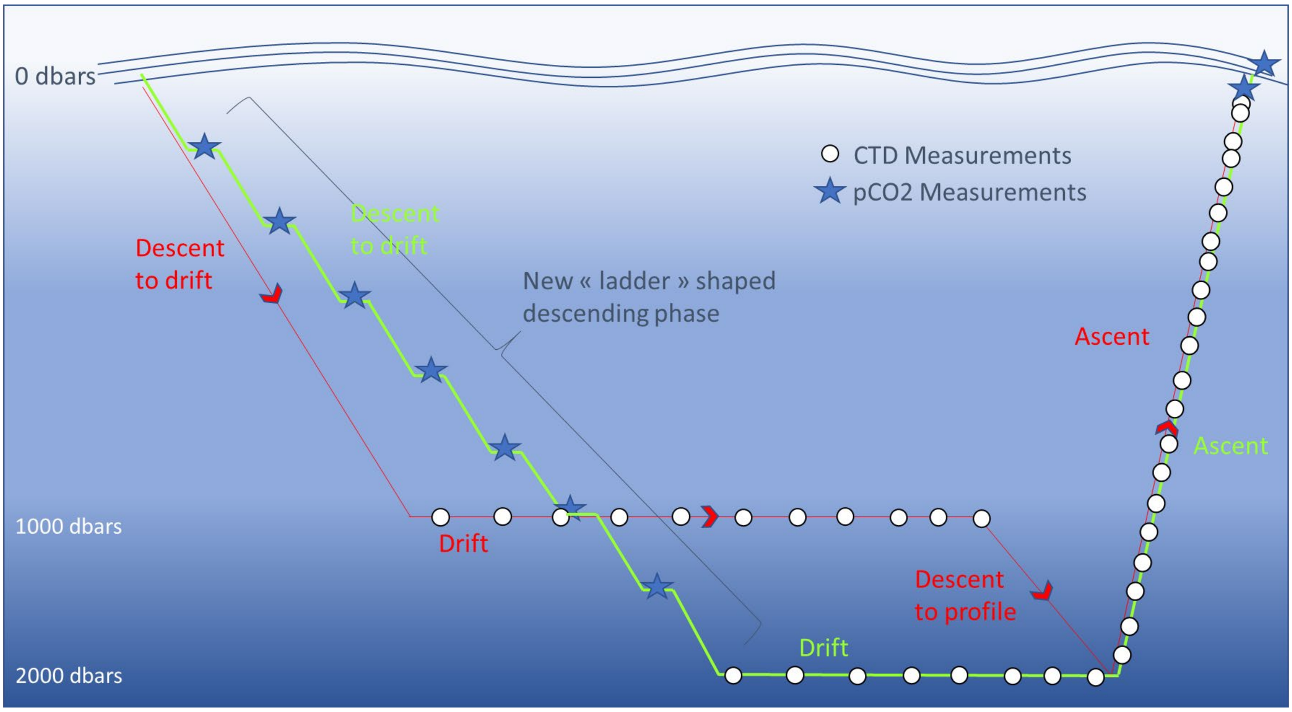



*Figure 5. Standard Argo profiling float cycling scheme (red) and modified one (green) allowing the sampling of pCO2 at surface and during the descending phase to drift level. Each step duration is about five minutes, above the mean $\tau_{63}$ time response of the Aanderaa 4797 pCO2 Optode.*

## 4 SUMMARY OF THE DEVELOPMENTS

Ref: IFREMER technical documents

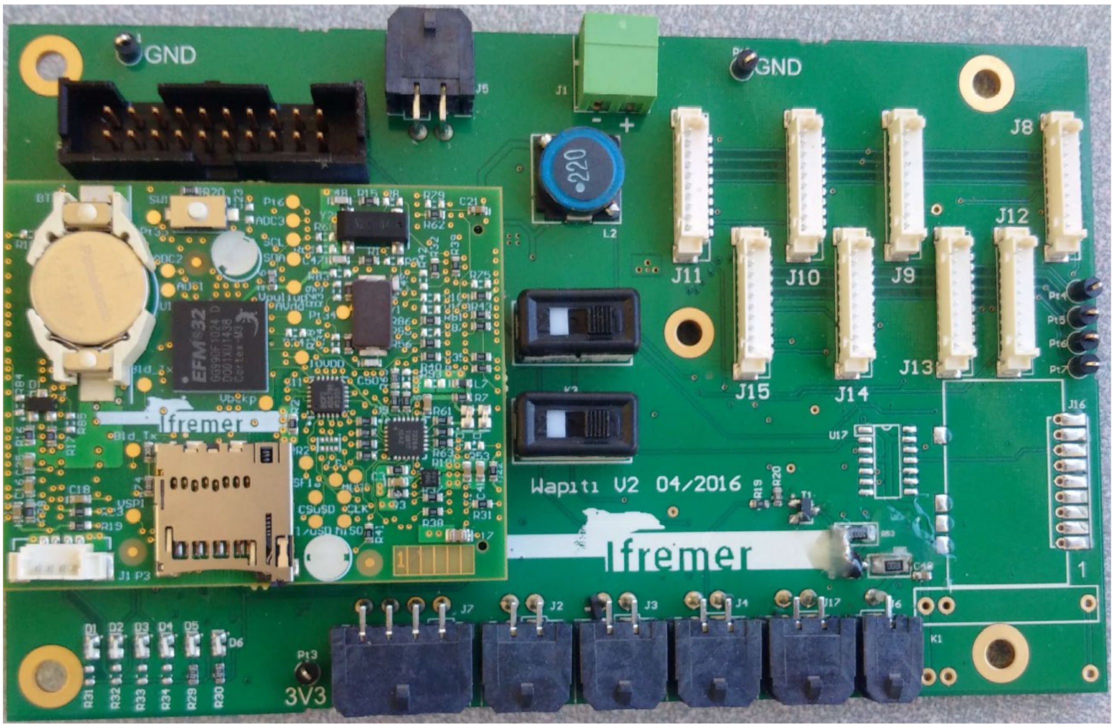
### 4.1 Hardware configuration

For the purpose of this development, the NKE Instrumentations PROVOR DO-I profiling float has been selected for its proven at-sea performance, its Iridium communications system allowing a full controlling of all float's parameters through remote connection, and its native ability to carry additional Aanderaa Optodes (Dissolved O2 or PCO2, object of the present study).

IFREMER R&D department has been strongly involved in the development of this platform, licensed for commercial activity to NKE Instrumentations company. The IFREMER engineers are fully qualified to develop new hardware/software features on the float, maintaining a local simulating environment and constantly developing the controlling boards for their own purposes.


*Picture 3. NKE Instrumentations PROVOR I model with the Aanderaa 4797 pCO2 Optode*

The addition of a new profile controlling as described in the chapter REF has required to add in the float's hardware an additional Printed Circuit Board for the sensor's handling, composed of two separate elements: The WAPITI board interfacing the science payload with the overall float's hardware controlling system, and a newly developed ALEES board for the specific tasks dedicated to data acquisition, storing, and satellite messages formatting.




*Picture 4. WAPITI and ALEES boards at the development stage in IFREMER*

The upgrade with this new board required some additional modifications on the float's hull:

1. Mounting of an external connector and inside wiring for Wapiti/Alees board upgrades

2. Upgrade of the Iridium Modem and its communication module

A schematic diagram of the communication flow between the three controlling boards is presented here below

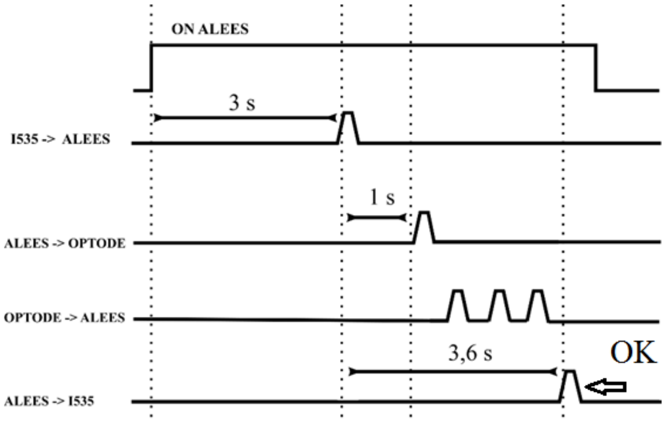



*Figure 6. Communication flow between the constituting elements of the pCO2 float's controlling system*

### 4.2 Software configuration

A complete set of new commands has been coded in the internal software for the pCO2 sensor handling:

1. Management of the sensor's sampling
2. Storing of the data in the internal memory
3. Formatting of the satellite messages

All commands can be operated through the satellite bi-directional link for modification of float's mission at sea.

## 5 ACCEPTANCE OF THE PROTOTYPE

### 5.1 Bench Simulation of the hardware/software system

Following the development of hardware and software system, a simulation environment has been set in order to test the features of the controlling boards and check that the complete processing chain is operational when exposed to a quasi-real profile of pressure.

Several profiles of Pressure from 0 to 1000 dbars have been applied to the assembly float/sensor and data files received through Iridium Communications have been analyzed.

Results showed that the complete acquiring/processing chain was working properly.

### 5.2 Unitary tests in IFREMER basin

The second validation step consists in an immersion of the profiling float equipped with its additional pCO2 sensor in a real environment to assess the functioning in sea-water.

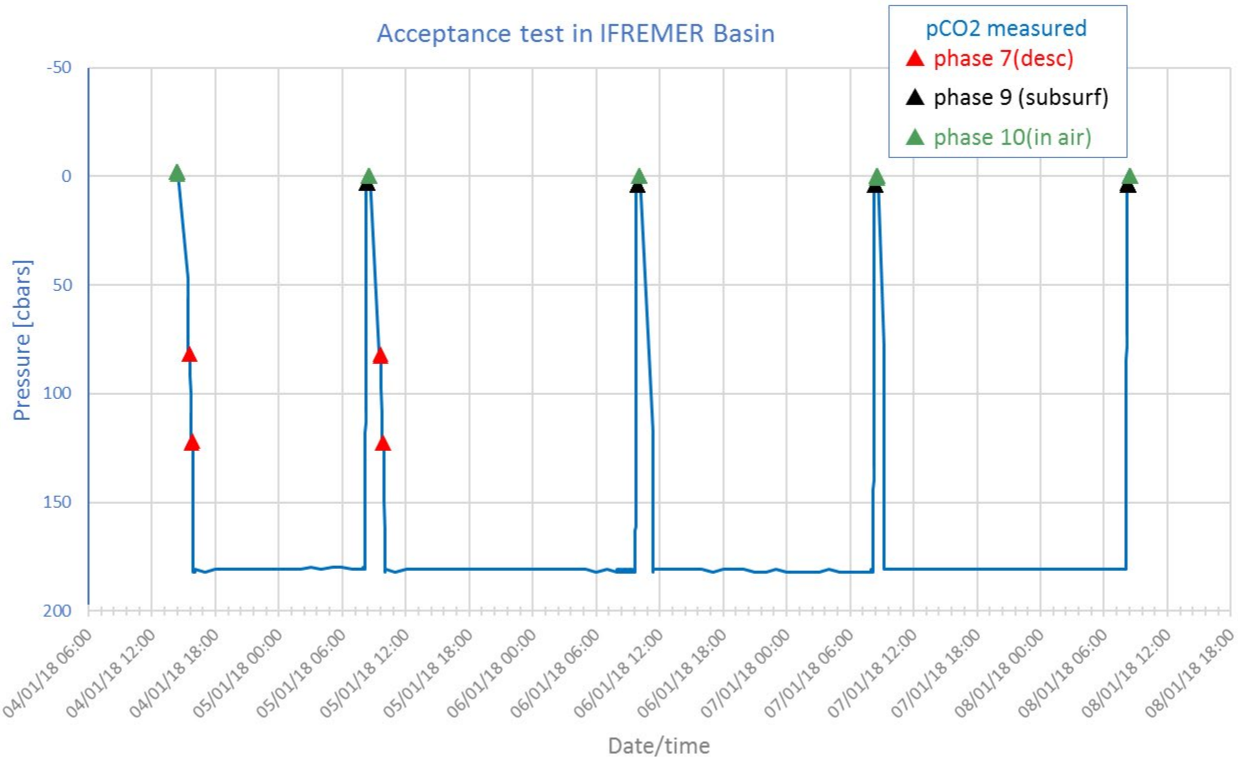
The prototype has been deployed in the IFREMER’s basin, with a depth capacity of 20 meters, and all systems have been tested: float’s buoyancy, sampling strategy, communication’s stream, data recovery and archiving on the repository.

In the basin, the float is freely sliding on a line tightened from surface to bottom (see Figure 6). In such shallow conditions, the float is able to reach the bottom without having to modify its buoyancy after having started its descent. As the solenoid valve is not in use during the whole descent to 20 dbars, no pCO2 measurement is available in a standard profile in the basin.

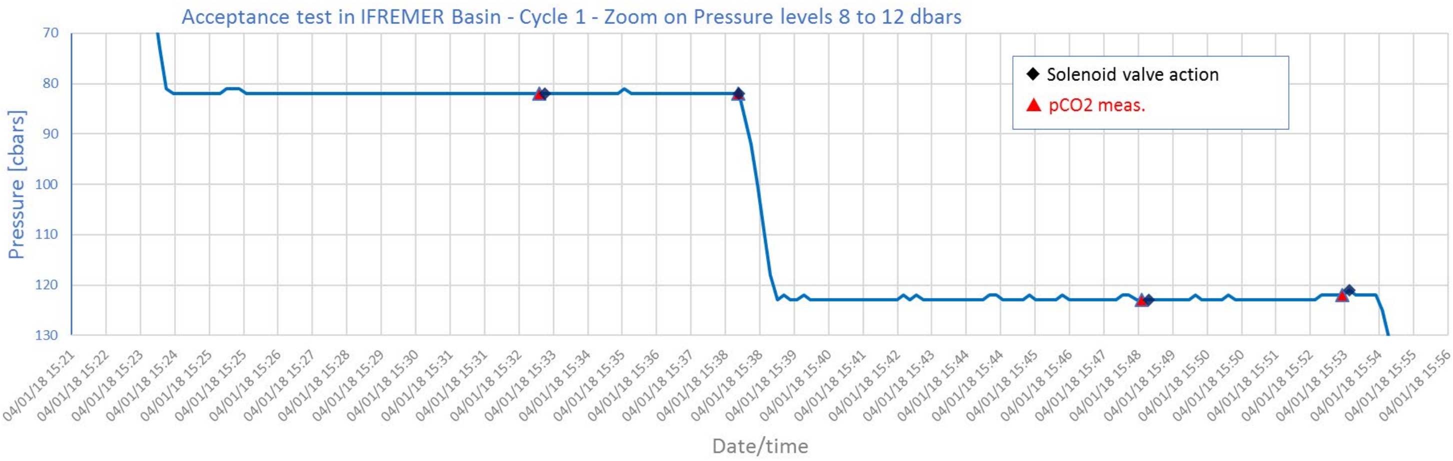
*Picture 5. The pCO2 profiling float prototype during the testing phase in IFREMER’s sea water basin*

Using the implemented grounding detection inside the float’s software allows us to overcome this issue: When for an unknown reason the float gets stuck during its descending phase, the grounding detection systems enables successive actions of solenoid valves aperture to decrease the buoyancy of the float. These actions are performed every 5 minutes.  During the tests, the float has been attached to a fishing line and two groundings have been stalled, one at 8dbars, one at 12 dbars, with a duration of 15 minutes each to ensure at least two solenoid valve actions from the float, and consequently 2 pCO2 measurements.

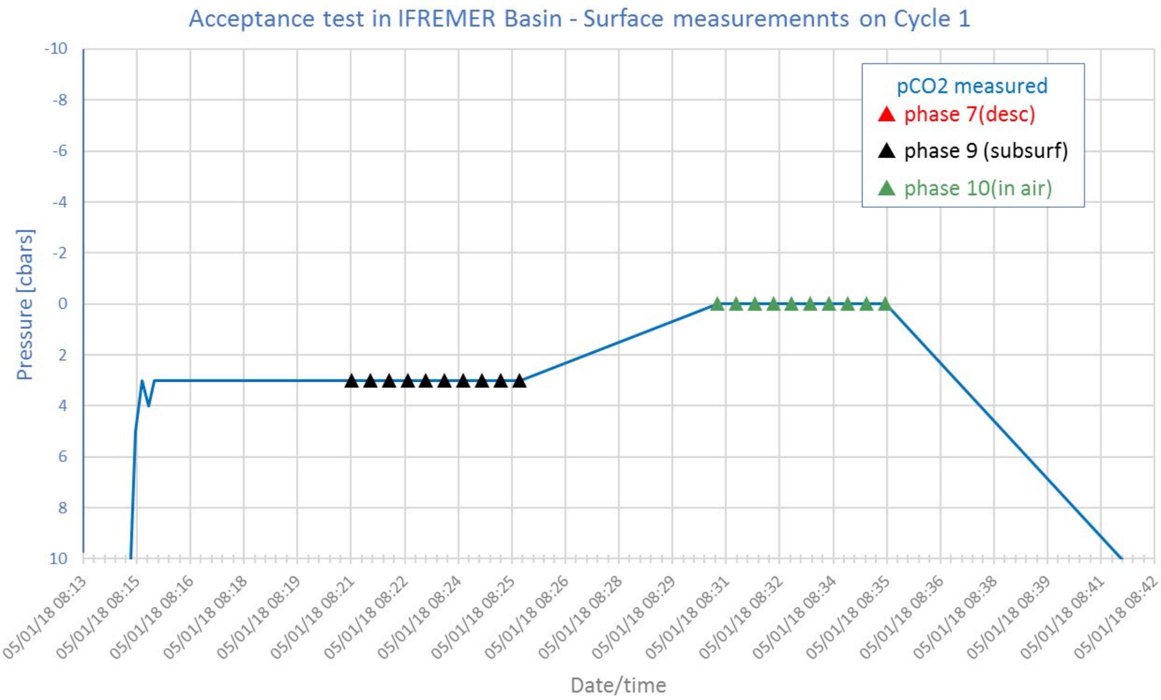
### 5.3 Acceptance tests results




The prototype float has been tested during 5 days and 4 cycles. During the cycle 1 and cycle 2, the float has been physically stopped at 8dbars and 12 dbars to allow pCO2 measurements.




The physical blocking of the float induces a sharp step in the measured pressure. After 15 minutes, two measurements of pCO2 are executed immediately followed by a solenoid valve action, demonstrating that the system follows the expected behavior




At surface, 10 measurements of pCO2 are correctly performed in both subsurface and surface layers.

The tests showed a nominal behavior and all expected characteristics have been validated, allowing to deploy the prototype during a real conditions field campaign.

### 5.4 Float *deployment* in real conditions in Mediterranean Sea – Dyfamed/Boussole Site

In collaboration with the Laboratoire d'Oceanographie de Villefranche (LOV/SU/CNRS) and the Institut de la Mer de Villefranche (IMEV/SU/CNRS), the prototype has been deployed during 5 days from the R/V TETHYS II coupled to the BOUSSOLE 200 / MOOSE / IADO-Teaching cruises.

The DYFAMED/BOUSSOLE site presents all the features requested for a short-term deployment of a prototyped profiling float. Although located at 5 hours of ship time from the LOV premises, the water depth is about 2500 meters allowing a nominal profiling scheme to be programmed. The BOUSSOLE Buoy is equipped with a continuous sampling system for all the Physical and Bio- Optical parameters at surface, including a CARIOCA (SU/CNRS/NKE Instrumentations) sensor measuring pCO2 maintained by the LOCEAN (SU/CNRS).

The monthly BOUSSOLE cruise maintains the buoy's systems (hardware and software), and performs high resolution ship borne sampling for CTD, Dissolved Oxygen (Winkler method), Total Alkalinity and ancillary parameters, allowing a refined assessment and validation of a profiling float's data cruising in its vicinity.

The validation deployment scheme and schedule are summarized in the figure below:

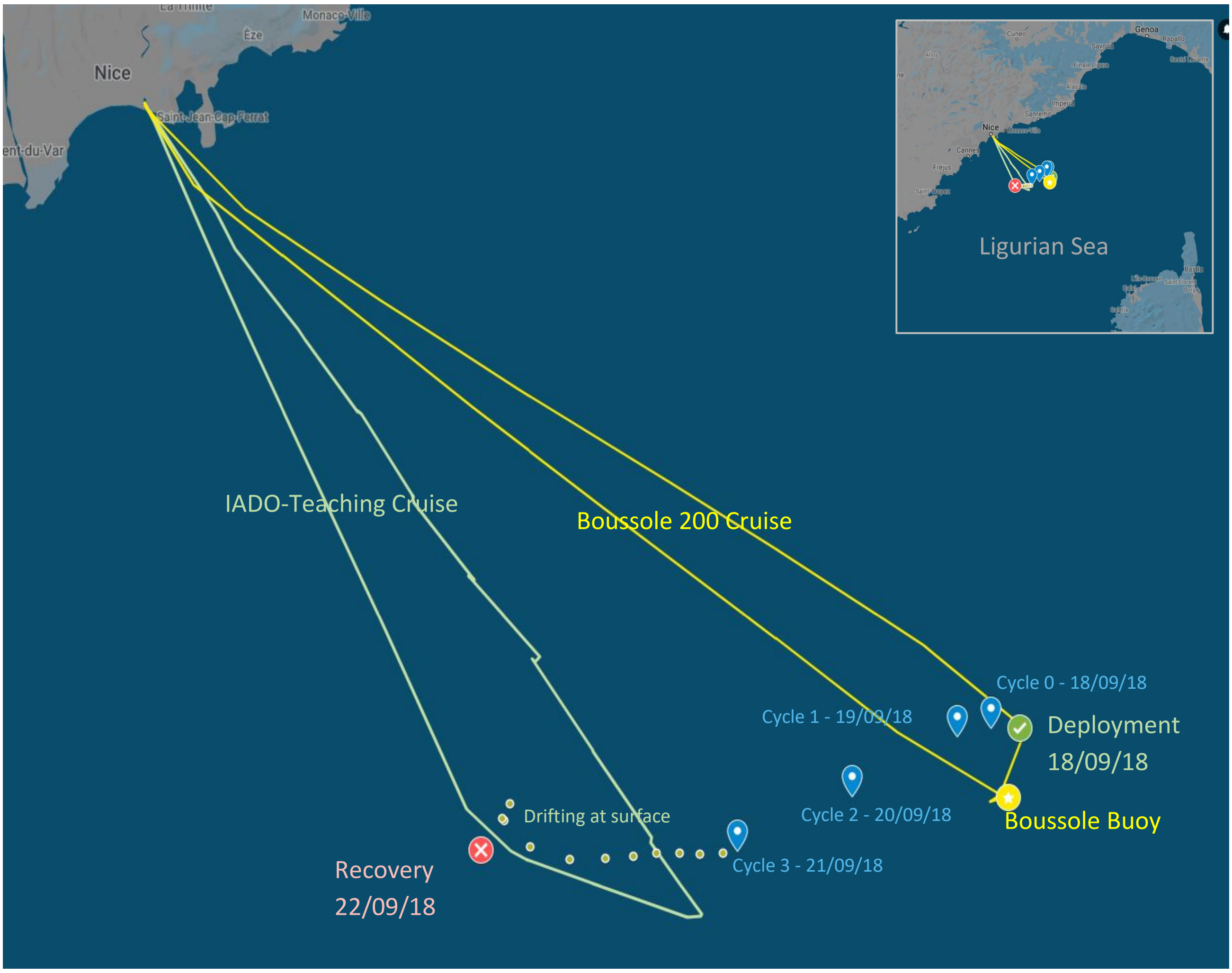



*Figure 7. Deployment and recovery of the pCO2 profiling float prototype in the Ligurian Sea during BOUSSOLE/MOOSE/IADO-Teaching cruise. Blue symbols are the float's location at the end of each corresponding cycle.*

*Picture 6. Deployment of the profiling float at BOUSSOLE site in Ligurian Sea*

The float has been deployed on 18th of September 2018 around 09:40, with almost perfect surface weather conditions. The first surfacing was programmed to the same day at 17:00 TU, and next surfacing where programmed with a 24 hours period. During its mission, some parameters have been changed through Iridium communications to ensure a surfacing at a time compatible with the recovery hour which depended on the R/V TETHYS II ShipTime.

Finally, four complete cycles have been performed (see Table 2), providing 4 descending profiles during which pCO2 sensor was ON, and 4 ascending continuous profiles Argo compliant but with pCO2 sensor OFF.

| Date | Time | Latitude | Longitude | Cycle # | Profile # |
|---|---|---|---|---|---|
| **18/09/2018** | 09:40 | 43.39958167 | 7.908315 | 0 | C0des |
| **18/09/2018** | 17:20 | 43.39903333 | 7.887403333 | 0 | C0asc |
| | | | | 1 | C1des |
| **19/09/2018** | 01:20 | 43.395105 | 7.86353 | 1 | C1asc |
| | | | | 2 | C2des |
| **20/09/2018** | 09:20 | 43.36663833 | 7.788541667 | 2 | C2asc |
| | | | | 3 | C3des |
| **21/09/2018** | 17:20 | 43.34071167 | 7.707081667 | 3 | C3asc |

*Table 2. Cycles performed during the Boussole200 field cruise*

The float has been recovered after 5 days at sea and 4 cycles on 22nd of September 2018.

## 6 TECHNICAL ANALYSIS

This first in-situ deployment was mainly aimed at verifying the functional behavior of the float with its new ladder-shaped descending profiling program.

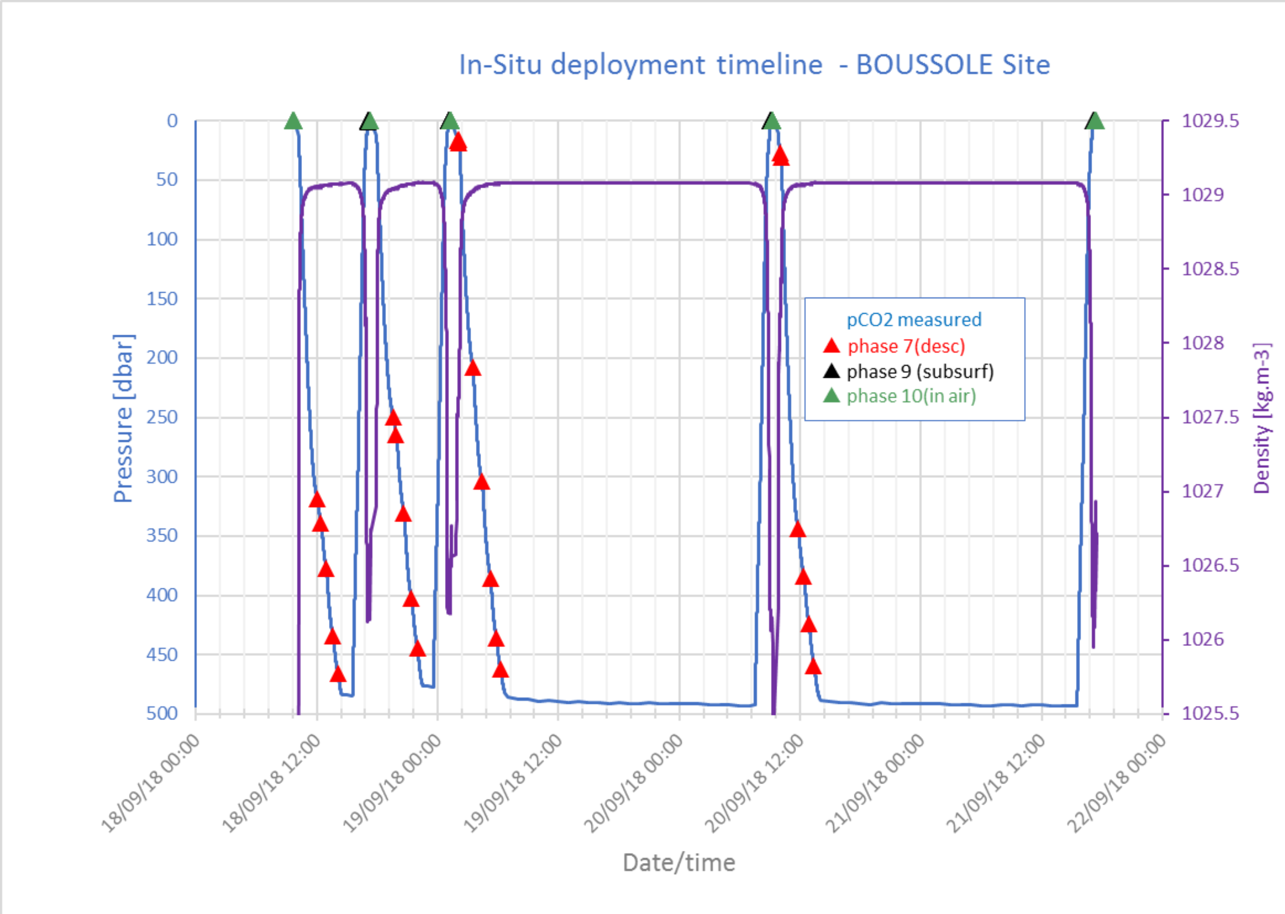


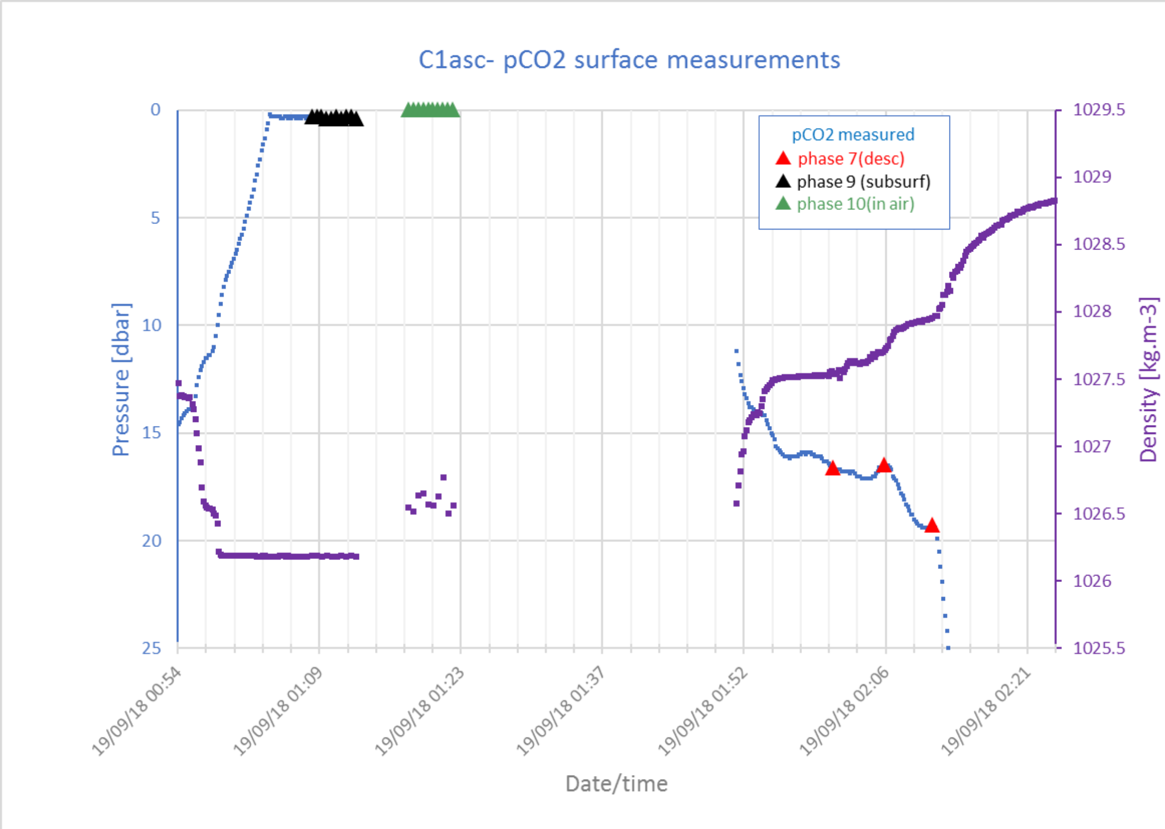

*Figure 8.In situ deployment timeline at BOUSSOLE site.*

## 6.1 Analysis of the coincident solenoid valve action vs. pCO2 measurement

The pCO2 measurements have occurred at each descending profile, and near to surface at each ascending ones as expected. The repartition of samples is not regular as explained in the paragraph 3, and not at same pressure levels across the profiles. On cycles 0 and 1, the first measurements occurred at depth (below 250 dbars) when on Cycles 2 and 3, some measurements have been done at about 2 dbars. Two reasons for this pattern:

- When diving, during the phase where the float is reducing its emergence, no measurement on the sensors can be done. This threshold is at 8dbars.
- A "learning" algorithm inside the float's software optimizes the emergence reduction in the first cycles after deployment. At deployment, the buoyancy of the float is not controlled besides the water density, and at cycle 0 the number of solenoid valve actions to ensure the dive is not representative of the entire float's mission. When the float comes back from its first cycle, its buoyancy at surface is theoretically the nominal one because the ascending control takes into account the environmental density, and the controlling system will then adapt the number of solenoid valve actions for diving starting form cycle 2.

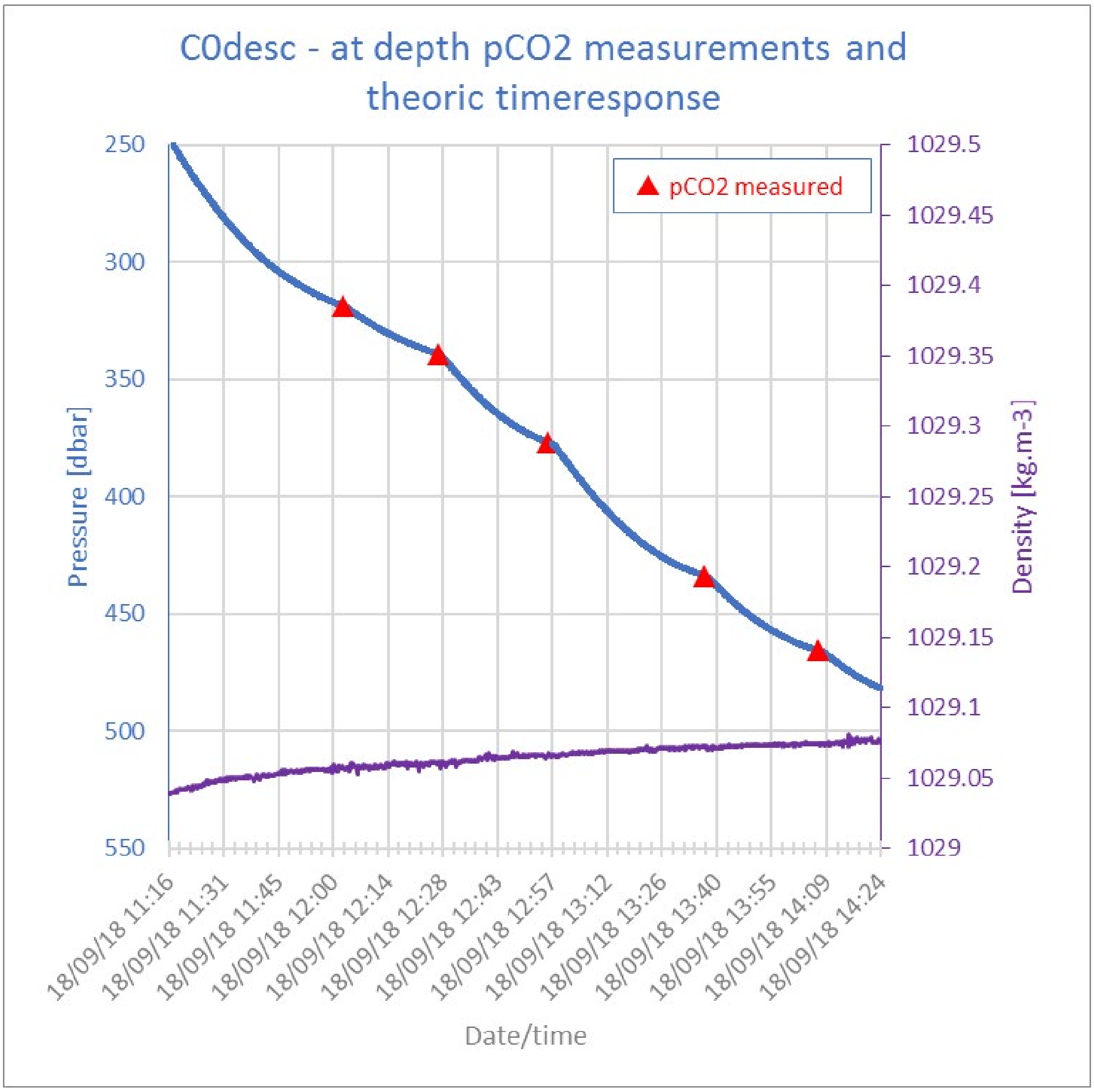
These two reasons combined explain that the float may leave the surface with a speed which can be varying, and that sometimes no solenoid valve actions are necessary before the float has reached depth, or solenoid valve actions have occurred above the emergence reduction threshold where measurements by sensors are not allowed.




At all surfacing, the float has performed both sub-surface pCO2 measurements and just above the surface. As an example, we have highlighted the float's pressure profile at Cycle 1 surfacing showing the distribution of 10 measurements at sub surface and above surface – which can be parametrized.

The CTD/ pCO2 measurements have been enabled at 11 dbar, and the density profile shows that a frontal area was crossed by the float. 3 solenoid valve actions have been needed to cross this front, inducing Three pCO2 measurements at the descent have been done at about 17 dbar.

### 6.2 Analysis of the relevancy of the pCO2 measurement sampling strategy




The highlight on the last part of the descending profile for the Cycle 0 shows that the shape, even if not strongly looking at a sharp ladder one, presents pseudo steps at the end of which a pCO2 measurement is done.

*Lifetime-based optode for measuring $pCO_2$*

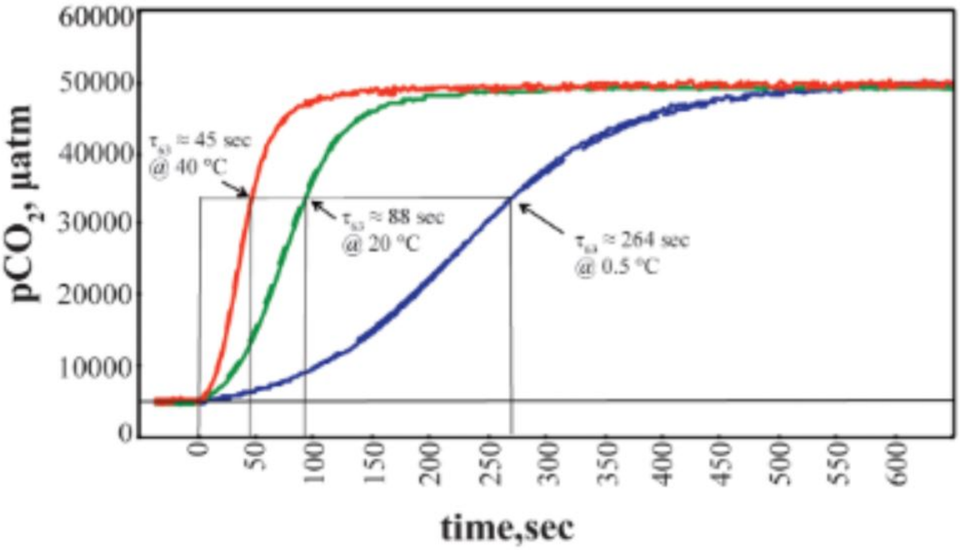
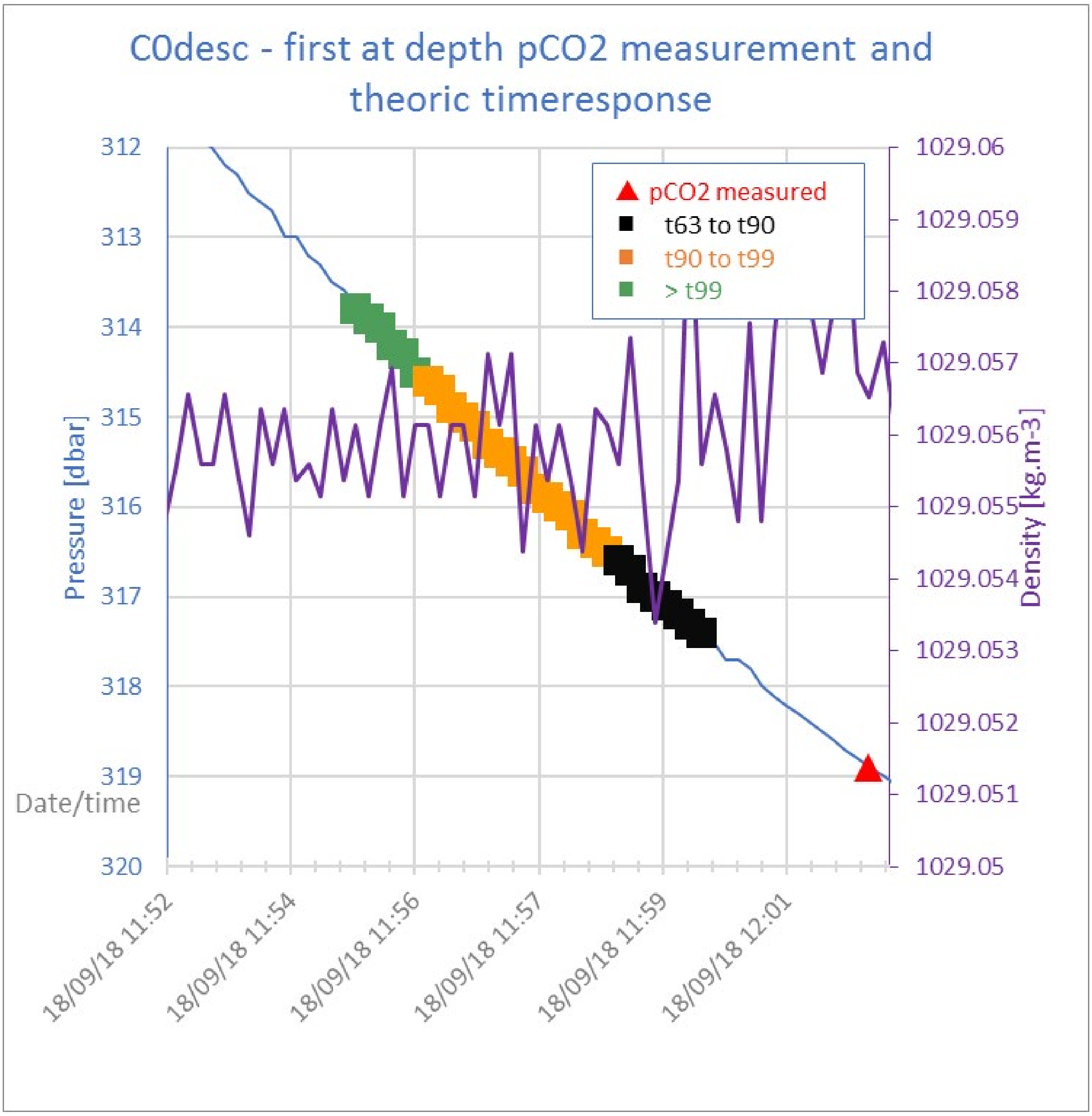



**Fig. 5.** The response times ($\tau_{63}$) of two $pCO_2$ sensors: S/N 11 (solid line) and S/N 12 (dashed line) obtained at 0.5 (blue), 20 (green), and 40°C (red).

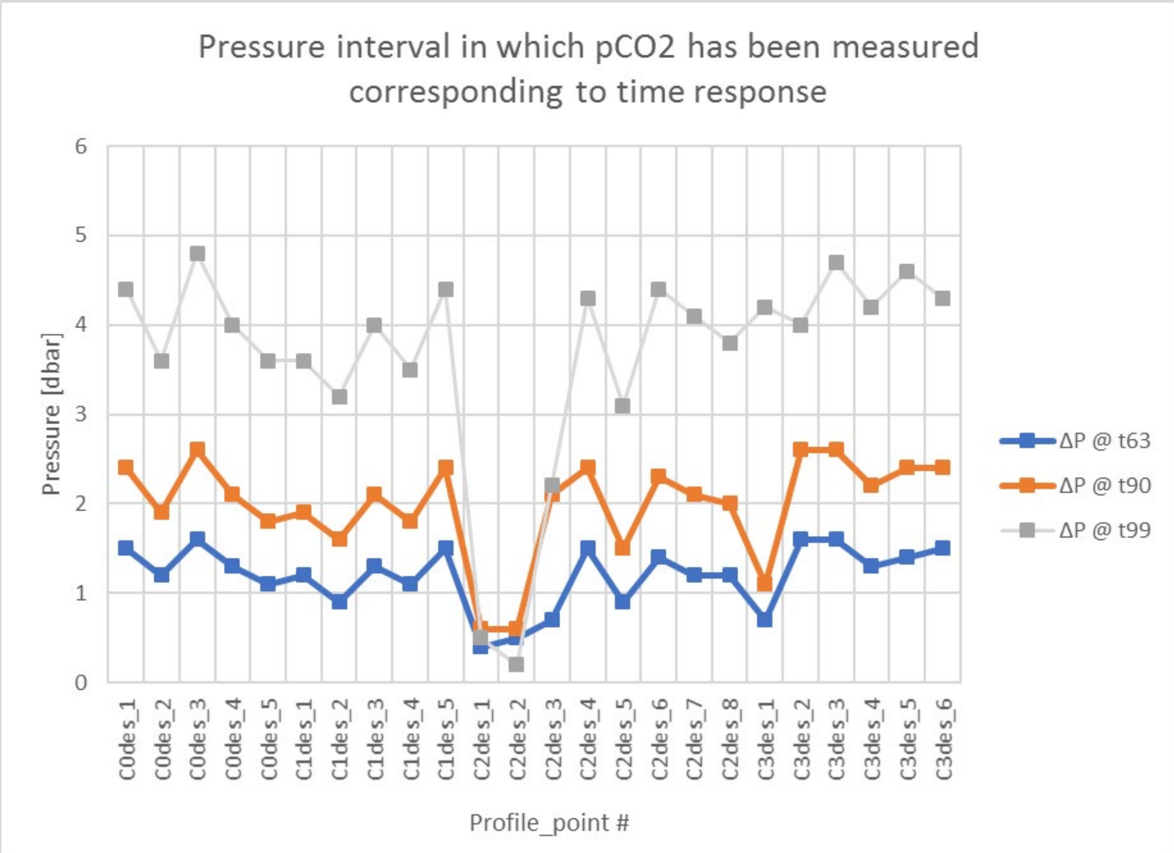
*Figure 9. from Atamanchuk et al, 2014. Derived time responses of pCO2 optodes in various Temperature conditions*

Derived from Atamanchuk et al., 2014, the theoretical time responses of the pCO2 Optode's foil have been assessed for the temperature of the measurement. Around 13°C, values are $\tau_{63}$ ~135s, $\tau_{90}$ ~215s and $\tau_{99}$ ~378s. The following figure shows the result for one of the measurements done at Cycle 0.




The density is almost constant in the $\tau_{99}$ interval (1029.056 kg.m-3) indicating a stable water mass from a hydrologic point of view. For this particular point, the pressure ranges enclosing $\tau_{63}$, $\tau_{90}$ and $\tau_{99}$ measurements are 1.5 dbar, 2.5 dbar and 4.5 dbar indicating an average speed of 1.2 cm/s, letting us consider that the float is stable .

The complete pressure ranges for the 24 points of pCO2 measurements are reported in the figure below




If we discard the points C2des_1, 2 and 3 and C3des_1 where measurements have been taken in the surface layer when float is not moving yet at its nominal speed, the average pressure range for the $\tau_{63}$, $\tau_{90}$ and $\tau_{99}$ is comprised between 1dbar for $\tau_{63}$ and 5 dbars for $\tau_{99}$.

This indicates that the minimum resolution for the characteristics of the first 500 meters of Mediterranean waters in September is 5 dbars.

### 6.3 Technical conclusions

The prototype demonstrates its ability to perform measurements at the descending phase with a pseudo-stabilized attitude, at least at depth.

The main weakness is the uncontrolled sampling scheme, and the lack of data acquired in the upper layers.

This could be overcome by adapting the float's technical parameters to reduce the solenoid valve action effects (reducing the max volume of each individual solenoid valve action), inducing a rise of SV actions for the float to dive, and subsequently a rise in the number of pCO2 measurements.

A Timeout based on the Time response vs. Temperature curve could be implemented in the float's controlling program allowing to let the float idle for the defined time before the pCO2 measurement and SV action when a SV action is required for the float movement.

Changing the controlling program of the float to be able to stabilize at pre-defined pressure steps would be an asset, but not foreseen in a mid-term schedule and probably implemented for the next generation profiling floats.

## 7 CONCLUSIONS

### 7.1 Future of pCO2 sensors for floats / commercial availability

Without a major break-through in $pCO_2$ sensing foil technology, no further improvement in $pCO_2$ optodes is to be expected. For measurement of the carbon parameter $pCO_2$ one therefore has to resort to the established planar membrane sensor technology with NDIR detection, which is not suitable for integration into BGC-Argo floats due to their current specifications (size, power demands).

The problem lies mostly with the properties of the sensing foil. A new foil type with largely improved properties is needed but apparently not within reach of the major manufacturers. This has led to severe delays with the development of a CONTROS $pCO_2$ optode up to a point where it remains questionable to the manufacturer, whether a $pCO_2$ optode product could actually meet the user demands concerning measurement performance.

### 7.2 Benefits for Global Argo Network of the pCO2 prototype development

The here presented prototype demonstrated that the float's technology is ready and able to integrate any type of additional sensor for the Argo network improvement, after minor changes in the float's hardware and adapted software / cycling strategy.

This prototype will be extensively deployed in the future months to provide a large amount of data, thus allowing to continue the collaboration with the sensor's manufacturer in order to improve the technical characteristics of the material, and to finally provide a suitable pCO2 sensor for the scientific community.

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