D1.2
Specification report of common test protocols and inter-comparison methodologies

WORK PACKAGE 1 – New Sensor technologies: innovation and services

LEADING BENEFICIARY: **EURO-ARGO**

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ABSTRACT

The content of the present reports highlights a specific use case specified at the beginning of ENVRIplus project, the measurement of the pCO_2 concentration from the air-sea interface to the bottom of the Ocean.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654182

The rationales of the relevancy of measuring pCO_2 concentration in the sea-water is exposed as being an extremely important parameter for the global Carbon cycle monitoring, and in particular the contribution of the Inorganic Carbon. During the ENVRIplus project timeline, several initiatives have been carried-out by the task partners to (1) assess the use of commercially available sensors for pCO_2 measurements and (2) trying to refine a common approach for across-network collaborations.

It appears that at the end of the exercise, no mature technology is suitable to cover all requirements needed for disparate networks, and that the Marine RIs have to start more cohesive synergies to achieve a common strategy for new sensors implementation.

Nevertheless, Interesting discussions have started inside this task consortium, and future collaborations are engaged to converge towards a future continuum strategy from sea-surface to bottom for the innovative sensors implementation.

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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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RATIONALES: the pCO_2 Use case

The ocean absorbs about 25 % of anthropogenic carbon dioxide (CO_2) emissions, 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. These changes are, however, quite variable regionally and with depth. 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 CO_2 sources and sinks exist in currently under sampled or even unsampled areas, which are undergoing rapid anthropogenically driven change and exhibit high vulnerability (e.g., increasingly ice-free Arctic Ocean, Southern Ocean, coastal seas).

The situation at sea surface is monitored on long term time series in sparse places of the global ocean, by using repeated oceanographic cruises where ships are equipped with surface continuum pCO_2 sampling systems. The produced data can be directly compared to atmospheric measurements of the pCO_2 concentration to assess the flux of inorganic carbon from atmosphere to ocean.

It becomes consequently obvious that data on carbon fluxes in the ocean is drastically lacking pCO_2 measurements in the water column. This is a cross RIs topic involving EUROARGO, EMSO/EUROSITES and the glider community of GROOM together with the marine component of ICOS and projects like JERICO. Ideally, once adopted in EUROARGO and international ARGO, a pCO_2 sensor will become a de facto standard in the marine domain. But the maturity of the sensor offer is not high enough to justify an integration in EUROARGO before a few years due to response time, energy consumption and calibration issues. That is why it is urgent that other RIs join their efforts with agreed methods and share of testing facilities, thus improving the sensing technologies to a level which could be mature enough for a global observation network such as the Argo program.

REVIEW OF THE EXISTING NETWORKS IN EUROPEAN MARINE DOMAIN

Surface Continuum

The surface measurements of pCO_2 concentration are ensured during oceanographic cruises from ships. The equipment and possibilities offered by modern units benefit to RIs such as ICOS marine; allowing both

- the under-surface sampling by using a continuous flow-through water pumping system connected to a bench water pCO_2 analyzer
- the above surface atmospheric sampling pumping the ambient air through gas inlets and analyzing the pCO_2 concentration with standard equipment as found usually on terrestrial stations.

Some difficulties remain for this shipborne measurement, as the crews have to control continuously that the samples are not contaminated by the activity of the ship (gas outlets from the engine, contamination of the surface water layer close to the ship's hull).

These activities are organized in common with EUROFLEETS RI, which maintain a database of available technical means for these surface measurements (water/air inlets, possibility to install dedicated deck containers) and provides detailed ship position along with local meteorological measurements allowing to post process the data to eliminate the potentially contaminated ones.

Moorings and bottom stations

PCO_2 concentration sensors are included on some long-term moorings across Europe, thus not being part of a standardized package for all of them.

The EMSO ERIC associated with the former FIX03 network advocates for a standardization of the mooring systems and performs test cases for the adjunction of new sensors on their water column and bottom stations. This activity was monitored at European level inside the EUROSITES project now integrated in the EMSO ERIC.

Autonomous platforms (floats/gliders/others)

In order to complement the historical shipborne sampling of key oceanic parameters, the emergence of reliable autonomous platform technologies during the last three decades have allowed to push the measurements to a globalized scheme, enabling real-time monitoring of the ocean to be used by ocean forecaster communities and modelizers for the global change assessment.

Autonomous Unmanned Vehicles, Gliders, Surface Wave Gliders, and Argo floats are now fully able to carry various sensors, potentially including the pCO_2 concentration ones.

The variability of spatial and temporal extension of each technology has induced the emergence of dedicated European Research Infrastructure or projects, with specific technological requirements for each of those:

- High seas and deep measurements down to 6000 meters are ensured by the Argo Program, and its European component EUROARGO ERIC implementing the profiling float's network for long term continuous sampling
- The GROOM project has centralized the European effort to harmonize the use of Gliders, suitable for short term sampling of the upper layer of the ocean and concentrating on meso-scale processes

- The JERICO project deals with the coastal sampling (Fix platform, Ferryboxes, etc), also implementing Gliders and exploring how surface autonomous vehicles such as Wave Gliders can be used on longer term deployments
- Although usually dedicated to other scientific purpose (acoustics, seismology, etc.), AUVs are regularly deployed from oceanographic ships and are able to integrate additional sensors for short term campaigns. The available material is monitored by EUROFLEET RI which enables access for common collaboration between the different scientific communities

Towards a collaboration across the European Marine RIs

The harmonization effort across the marine domain European RIs sampling strategy can be balanced as compared to the atmospheric domain one to understand the technological difficulties inherent to the harsh marine environment.

The Atmospheric domain RIs have managed to implement a common and global way to monitor the atmosphere essential variables defining standard instrumentation and minimal requirements for a sampling station settlement. Because the human presence is possible almost at every time on-site, ICOS, ACTRIS and IAGOS are able to deploy the same instruments even in such various environments as ground stations, planes, meteorological balloons or ships, ensuring the maintenance, the replacement of consumables, allowing cross-calibration campaigns without disturbing the time series.

The Marine domain European RIs are facing much more difficulties because of inherent conditions to the Ocean sampling: continuous or regular human presence is not possible; sampling above surface, at the air-sea interface or into the water column until the bottom of ocean requires specific design of the instrumentation to face to issues such as corrosion, resistance to pressure, impossibility to replace the consumables, energy and sizing concerns. Although each single RI or project has defined some best practice procedures to harmonize the technological implementation of instrumentation on their own platforms, across RI collaborations have not really converged towards a global strategy to ensure a complete continuum from surface to bottom of the Ocean.

Some of the specifications of each component of the marine domain sampling area are described in the following chapter.

TECHNICAL NEEDS/POSSIBILITIES FOR EACH NETWORK

TRL variability

Depending on Technology Readiness Level (TRL), the evaluation and comparison of available instrumentation is done differently.
It is also different from one community to the other, one RI to the other. In the table below, the position of each infrastructure, limiting the reflection to the RIs involved in the pCO_2 concentration Use case and to sensor developments is presented in a summarized way:

TRL	EUROARGO	GROOM	ICOS Marine	EMSO	JERICO
1 to 3	Discarded	Discarded		Discarded	Bibliography
4	Awareness	Awareness	Awareness	Awareness	Lab evaluation
5	Awareness	Awareness	Evaluation in simulated conditions		Evaluation in simulated conditions
6	Awareness	Awareness		Intercalibration	Intercalibration
7	Individual short-term tests	Field tests	Field tests/ Cruises	Long term testing	Field tests
8	Field tests – comparison of prototypes	Individual implementation		Intercomparison Exercises (FixO3-FCT and ACT reference[1])	Intercomparison Exercises (FCT/ACT)
9	Intercomparison at large scale (reliability, data quality …)	Intercomparison is practiced by users independently or by cooperation with providers	Calibrations - Labs are complying or not with the "ICOS label"[2]	Intercomparison not practiced yet (except DONET and ONC)	Large scale evaluation (reliability, Data quality …)

The purpose of the present report is to address TRL7 and 8 for its marine use case.

The current practice adopted by all the partners is:

- either oriented by a will to increase the TRL of one sensor (in a away included in the ENVRI PLUS WP1 global scope in term of metrology harmonization, collaboration with industrial partners)
- or to prove the potential of a specific technology to be used with respect to the existing offer on the market
- or to compare the existing solution to choose one of them or to provide recommendations in order to use several with proper correction to meet common infrastructure's needs (ENVRI PLUS WP1 1.2-Use case 1 – pCO_2 sensing tentative).

Derived from the Technology Readiness Level requirement for each RI, one can specify the minimal features for sensors as described below.

Sensor's size/volume

The requirements in term of size/volume of sensors are conditioned by the load capacity of the carrying platform in which the instrument will be integrated:

- Shipborne campaigns: a ship lab can be assimilated to a terrestrial station where all sizes of instruments can be installed

[1] Forum for Coastal technology – http://archimer.ifremer.fr/doc/00125/23606/ - attempt to implement a similar organization as the Alliance for Coastal Technologies - http://www.act-us.info/
[2] Bert Gielen - ICOS station labeling 2016 ICOS BELGIUM CONSORTIUM STUDY DAY – 04.05.2016 - Gembloux

- Moorings and bottom stations are somehow limited for the size/weight/volume of integrated instrumentation, but these characteristics can easily be compensated by the adding of calculated buoyancies to reduce the impact on the structures.
- Gliders, Wave gliders and AUVs cannot stand with the integration of large instrumentation, but the sizing of the platform allows although medium sensors to be carried
- Profiling floats is the most restrictive platform in term of sizing of sensors. Being light and small ones, they require extremely reduced casings to deal with their sampling scheme based exclusively on the volume variation.

Sensor's Energy budget

The power draw of the sensors is always adapted to the available energy on the carrying platform:

- Shipborne campaigns: on-board energy can be provided almost without any limit from the power stations,
- Moorings and bottom stations can stand with large battery containers, some of them may also be powered with surface solar panels when a surface buoy is available (PIRATA type moorings)
- Gliders and AUVs may embark middle size battery packs and can deal with short term high consuming sensors; Wave gliders usually hold a solar panel allowing to charge continuously a middle range battery pack.
- Profiling floats stored energy is defined at the float manufacturing, and cannot be easily modified without a complete re-design of the platform. Thus only low consuming sensors can be integrated, and their current draw has to be fully controlled on order to maintain the global lasting of the entire system.

Sensor's Depth rating

Depending on the depth at which the carrying platform is operated, the design of the sensor has to be adapted in term of material and shape used for its casing, and resistance of all the accessories towards the pressure (cables, connectors, etc.)

The requirements in term of size/volume of sensors are conditioned by the load capacity of the carrying platform in which the instrument will be integrated:

- Shipborne campaigns: no specific requirements as equipment will be used at atmospheric pressure
- Moorings and bottom stations: variable depth rating are affordable since instrumentation can be installed at sub-surface, in the water column or at the bottom of the ocean. Once deployed, the instruments are not changing their immersion thus avoiding the dynamic effects of pressure cycling which can degrade the behavior of casing components, and rending easier the design of casings
- Wave gliders stay at surface of the ocean, and the instrumentation is stalled at some meters below the sea surface. Although waterproofness has to be ensured, the pressure levels reached do not required a strong pressure rate for sensors casings.
- Gliders, and AUVs are usually dedicated to an assessed depth rarely exceeding the first 1000 meters below surface. But these platforms have a dynamic sampling scheme, climbing and diving in the water column continuously, and not limited to the surface layer.
- Profiling floats continuously profile from sea surface to the bottom of the ocean. The sensors they carry thus require the most restrictive depth rating, combined with a highly dynamic sampling scheme.

On-site Maintenance

Depending on the possibility to access the platforms for a human intervention, te technology used may vary in term of cleaning against the bio-fouling, handling of the potential corrosion, replacement of consumables (chemical reactants, cables, connectors, batteries), turn-over of the complete sensing equipment

- Shipborne campaigns do not present any issue as skilled crew is always on duty to monitor and maintain the instrumentation
- Moorings and bottom stations are usually visited once to twice a year (and more often for coastal ones) allowing maintenance on all the aspects
- Gliders and AUVs are recovered after some weeks at sea and can then be maintained to a full operational state;
- Wave Gliders and Profiling floats are deployed on a partially autonomous way for the first, and a full one for the latter. Wave Gliders are operating at surface where environmental conditions can be harmful for the platform structure, and when deployed in open sea are not easily reachable for maintenance. Profiling floats are released in the open ocean with no scheduled human maintenance, requiring the strongest and most reliable technologies to fulfill their pluri-annual sampling program.

Conclusion on the equipment engineering

The characteristics exposed here above show clearly how the marine instrumentation requires various features depending on their deploying method. Each marine domain RIs addresses the constraints for their activity and new sensor developments are usually limited to the highest constraints they have to meet. The equipment manufacturers dedicate their developments to one or another use, concentrating on specific market without a global concern to propose fully interoperable instrumentation.

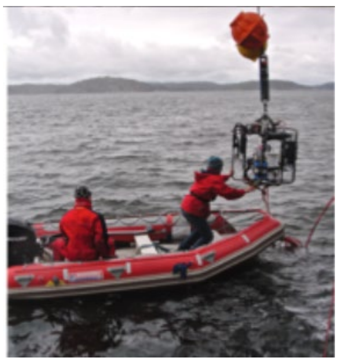
All these constrains derive to a compartmented market for sensors, increasing the difficulty for a complete cross RI assessment and use of unique sets of equipment.

INDIVIDUAL RIs INTERCOMPARISON EXERCISES

Nevertheless, conscious of the necessity to address the continuum of measurements from bottom to surface, each individual RI through its composing research institutes has carried out individual tests to improve this tremendous goal.

EMSO/FIXO3 inter-comparison experiment

In April and May 2014, a complete set of instrumentation for pCO_2 concentration and pH has been tested on a mooring at the Koljoefjord observatory (Norway) – [FIXO3_Work Package 12 Deliverable 12.1]:



- 4 different pCO_2 technologies from 5 manufacturers.
- Different pH technologies from 5 manufacturers.

The tested sensors are listed here below:

- Aanderaa Seaguard pH (optode), 2*pCO_2 (optode)
- Contros pCO_2 (IR) old
- Franatech pCO_2 (laser)
- Kochi Univ./Kyushu Univ. 2*pH (electrochemical)
- Kyushu Univ. 2*pH (ISFET), 2*pCO_2 (ISFET)
- PSI pCO_2 (IR) new
- PSI pCO_2 (IR) old
- Sensorlab pH (colorometric)
- YSI EXO_2 pH (electrochemical)

The results of the exercise showed that the instruments tested, disparate in their technological readiness development, behaved with varying success. We report here the results for the pCO_2 concentration sensors:

The Multiplexer failed to deliver any data on-line, partly failed to deliver power to sensors (see below) and disturbed the original Seaguard/RDCP monitoring system that has been in operation at this site since April 2011.

It is believed that apart from the periods with low voltage sensors should have received stable power, and consumption increased and decreased due to normal sensor operation.

- Seaguard with pH and 2x pCO_2 (and O_2 and T, and pressure): full set of data, cable power+battery backup. Interval: 1 min
- Pro-Oceanus PCO_2-pro CV (the small new Pro-Oceanus): full set of data. Cable power only, received enough power during the outages. Interval: 30 min
- Pro-Oceanus PCO_2-PRO (the big old Pro-Oceanus): logging system was overwriting old data when the sensor was restarted after power outages. Data available for the last 8 days only. Cable power only. Interval: 60 min
- Franatech pCO_2: data read out of the Multiplexer, from April 09-29, and May 05-08. No data after May 08. Cable power only. Interval: 1 s
- Japanese 2x ISFET pCO_2: standalone on batteries. Nobody came to participate the recovery from Japan, and no software was available to read off the data. The sensors were sent back to Japan to Kiminori, who will download data from the sensor memories. Interval: 1 Min (ISFET).
- Contros pCO_2: good data, data available in the sensor internal storage memory, excluding the periods of 12 power outages. Run with power from cable only. Interval: 100 s. Automatic zeroing 2 times per 24 h.
- RCM9 current meter, standalone on batteries, to measure background current, oxygen, salinity, temperature 1-1.5 m above the frame: full set of data. Interval: 10 min

According to pressure readings (available from RCM9, Seaguard and YSI EXO_2), the frame with sensors was sitting at around 4.4 m depth, while reference samples for Alkalinity, DIC and pH were taken at 8 m. Due to this quality of reference data can be a problem.

From the survey it was concluded that many of the commercially available instruments had a high-power demand and required cabled power to operate at a fixed observatory for more than 1 month with a good time resolution of the measurements. All the instruments supported a serial communication protocol and data communication from multiple sensors could be arranged through the serial multiplexer.

This study showed that working with a number of instruments from different manufacturers such issues as compatibility and cross talk should be carefully addressed. Simple design of the benches and straightforward data acquisition and transmission scheme required thorough adjustments both within the benches and between the benches and the existing cabled observatory in the KoljoFjord. A pre-deployment is highly desirable and recommended to make sure that the benches operate according to specifications.

GEOMAR Ship-borne Inter-comparison campaigns

At-sea comparison of performance of KM CONTROS HydroC pCO_2 sensor against General Oceanics 850 pCO_2 reference system:

During R/V SONNE Cruises SO234/2 and SO235 (July/Aug. 2014), a HydroC pCO_2 sensor was operated continuously on pumped surface seawater in a flow-through tank. The sensor-based pCO_2 measurements agree to within 3 µatm with the reference system (Fig. 4). This confirms earlier findings that measurements with the HydroC pCO_2 sensor can be made with an estimated accuracy of ≤ 3 µatm. Such high quality, however, is only achievable under the following tightly constrained operation conditions: (i) the sensor has to undergo individual multi-point calibration (e.g., by manufacturer) prior to field deployment, (ii) the auto zero function of the sensor has to be used frequently (i.e., at least every 12 h) throughout the deployment to correct for the zero drift, (iii) the sensor has to undergo a post-deployment calibration under the same conditions as the pre-deployment calibration, (iv) the span (response) drift of the sensor has to be corrected for by using the pre- and post-deployment calibration results and by making the correction factor itself a function of the zero drift of the sensor.

Significant results

The following results can be considered robust and significant:

- NDIR-based pCO_2 sensors with planar membrane equilibration (KM CONTROS HydroC pCO_2 sensor) can be operated in pumped underway mode (VOS application) to an accuracy within ±3 µatm following stringent operation practices and thus approach the accuracy achievable with classical equilibrator-based pCO_2 systems;
- NDIR-based pCO_2 sensors with planar membrane equilibration (KM CONTROS HydroC pCO_2 sensor) can be successfully integrated into autonomous platforms which have less stringent power limitations such as moorings, short-deployment surface drifters and the Wave Glider.
- NDIR-based pCO_2 sensors with planar membrane equilibration (KM CONTROS HydroC pCO_2 sensor) cannot easily and without major compromises be integrated into platforms such as floats and glider which have tight power and hydrodynamic limitations. For these platforms, currently no fully satisfactory pCO_2 sensor exists and we have to wait for the pCO_2 optode technology to further develop and mature.

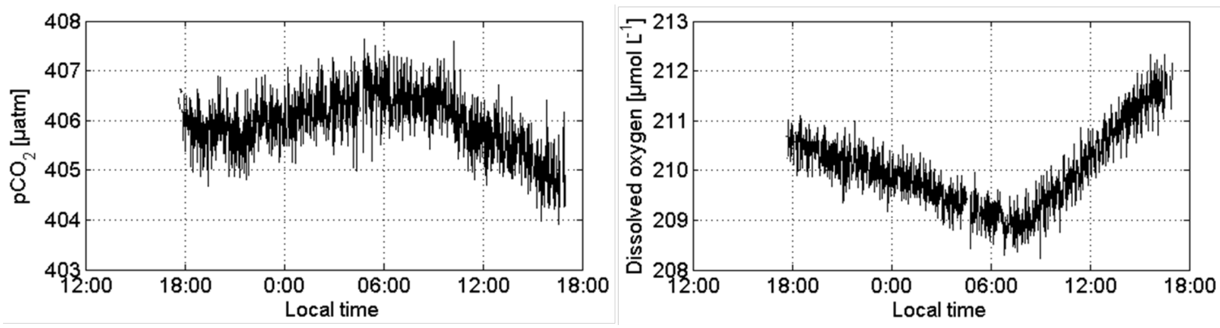


Figure 1. *Mixed layer diel cycles of pCO_2 (left) and O_2 (right) observed with a Lagrangian surface-tethered drifter with biogeochemical sensor package (S, T, pCO_2, O_2, nitrate, chlorophyll) in the southern Indian Ocean during R/V SONNE Cruise 234/2 (July 2014). The pCO_2 data show a precision of <0.3 µatm which allows to resolve diel cycles of less than 2 µatm.*

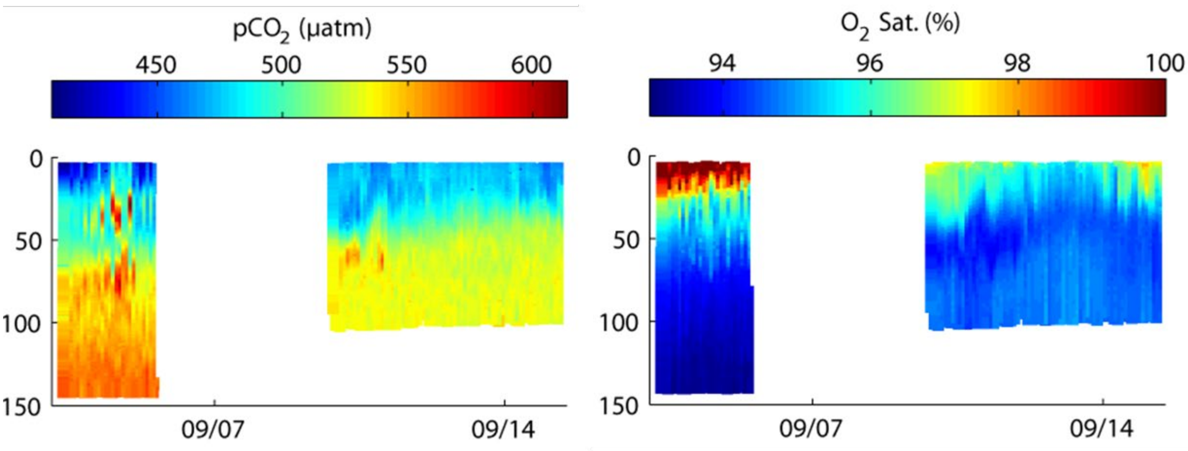


Figure 2. *Results from two test deployments of the moored submersible winch system with biogeochemical profiler (T, S, O_2, pCO_2, chlorophyll) in the Koster Fjord near the Sven Lovén Centre for Marine Infrastructure in Tjärnö/Sweden in Sept. 2014. The instrument was set to frequent profiling from 140 m/100 m to just below the surface. A trial deployment at the Cape Verde Ocean Observatory in the tropical Atlantic (17.6°N, 24.3°W) in September 2015 was not successful. The next deployment of a mechanically improved system is planned for Jan. 2017 in Cape Verdean water.*

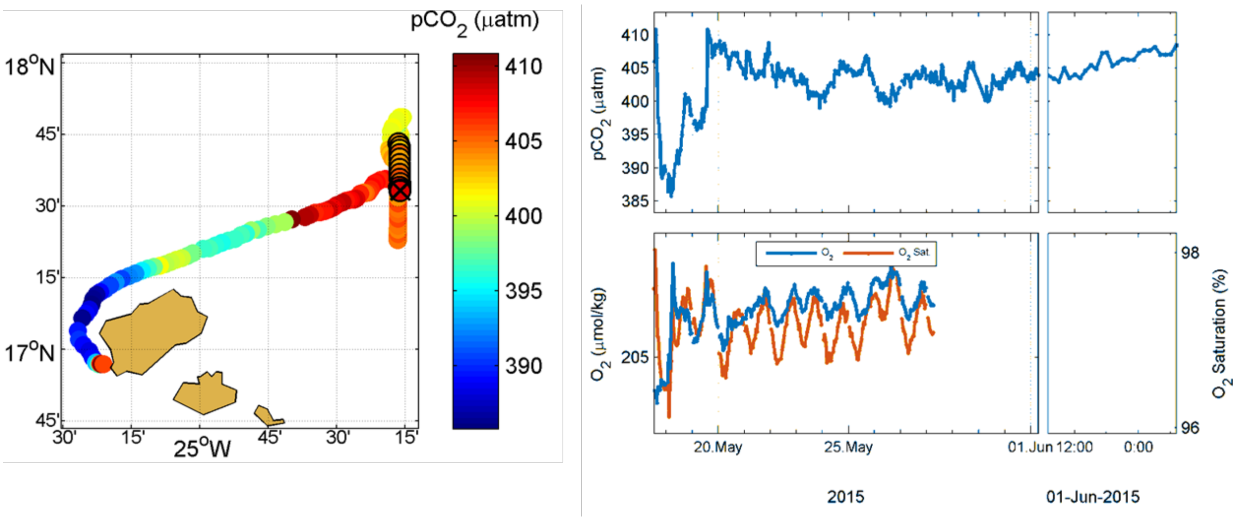


Figure 3. *Results of a successful deployment of the Liquid Robotics Wave Glider with biogeochemical sensor package (T, S, O_2, pCO_2, gas tension, chlorophyll) in the open ocean around the Cape Verde archipelago off West Africa in May/June 2015. The Wave Glider was deployed near the island of Santo Antão and programmed to sail to the Cape Verde Ocean Observatory (17.6°N, 24.3°W) where it performed repeated short meridional sections.*

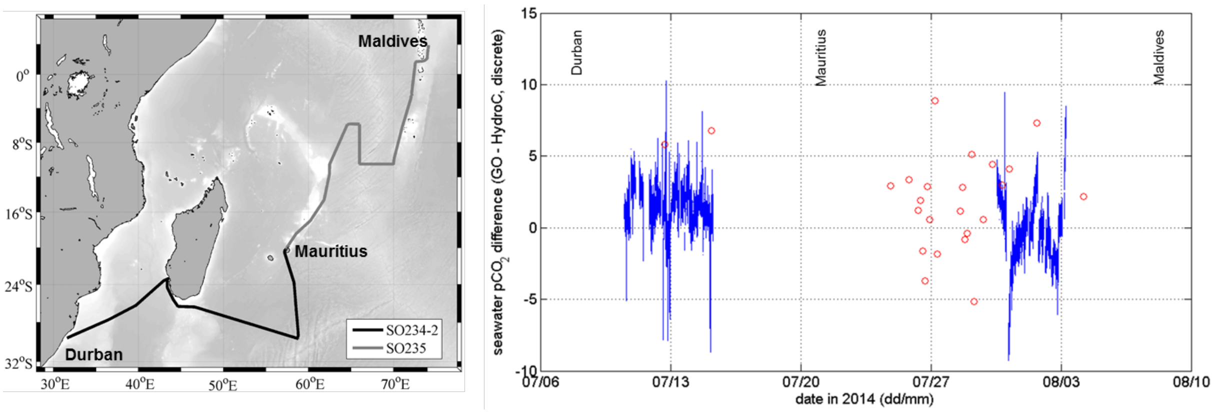
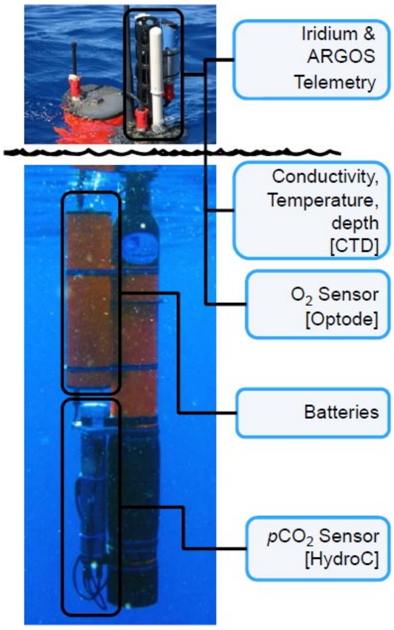


Figure 4*. Comparison of pCO_2 data acquired in underway mode with two different pCO_2 instruments (GO 8050 pCO_2 system (reference) and KM CONTROS HydroC pCO_2 sensor) during the R/V SONNE Cruises SO234/2 and SO235 from Durban/South Africa via Port Louis/Mauritius to Malé/Maledives (July/Aug. 2014). The pCO_2 sensor*

data agree better than 3 µatm with both the reference pCO_2 system and the pCO_2 calculated from discrete DIC and TA measurements.

GEOMAR Implementation of pCO_2 measurements on autonomous platforms:

A first attempt to implement a PCO_2 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 pCO_2 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.



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. 5.A and 5.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 7th June 2016 in the Mediterranean Sea off the coast of Villefranche-sur-Mer. This test profile can be seen in Fig. 5.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)

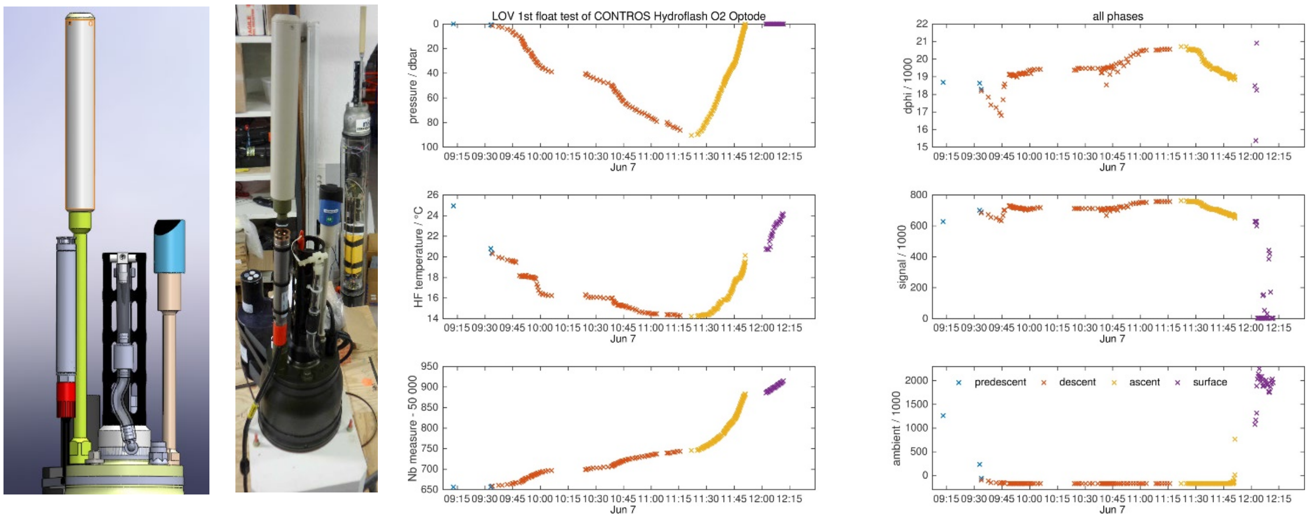


Figure 5. *(A) Schematic arrangement of the CONTROS HydroFlash® O_2 optode next to the CTD and Aanderaa optode on a PROVOR float. (B) Successful proof-of-concept float (PROVOR) implementation of a CONTROS HydroFlash® O_2 optode as a precursor for further work on pCO_2 optodes. (B) First profile of the 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 *p*CO_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. 6.A schematically shows all underway measurements during M133 in which the *p*CO_2 prototype was integrated (flow line 5d, red box). Optical, continuous *p*CO_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 *p*CO_2 optode sensor (model 4797) was installed in the flow-through chamber SOOGuard. Part of the full setup is shown in Fig. 6.B.

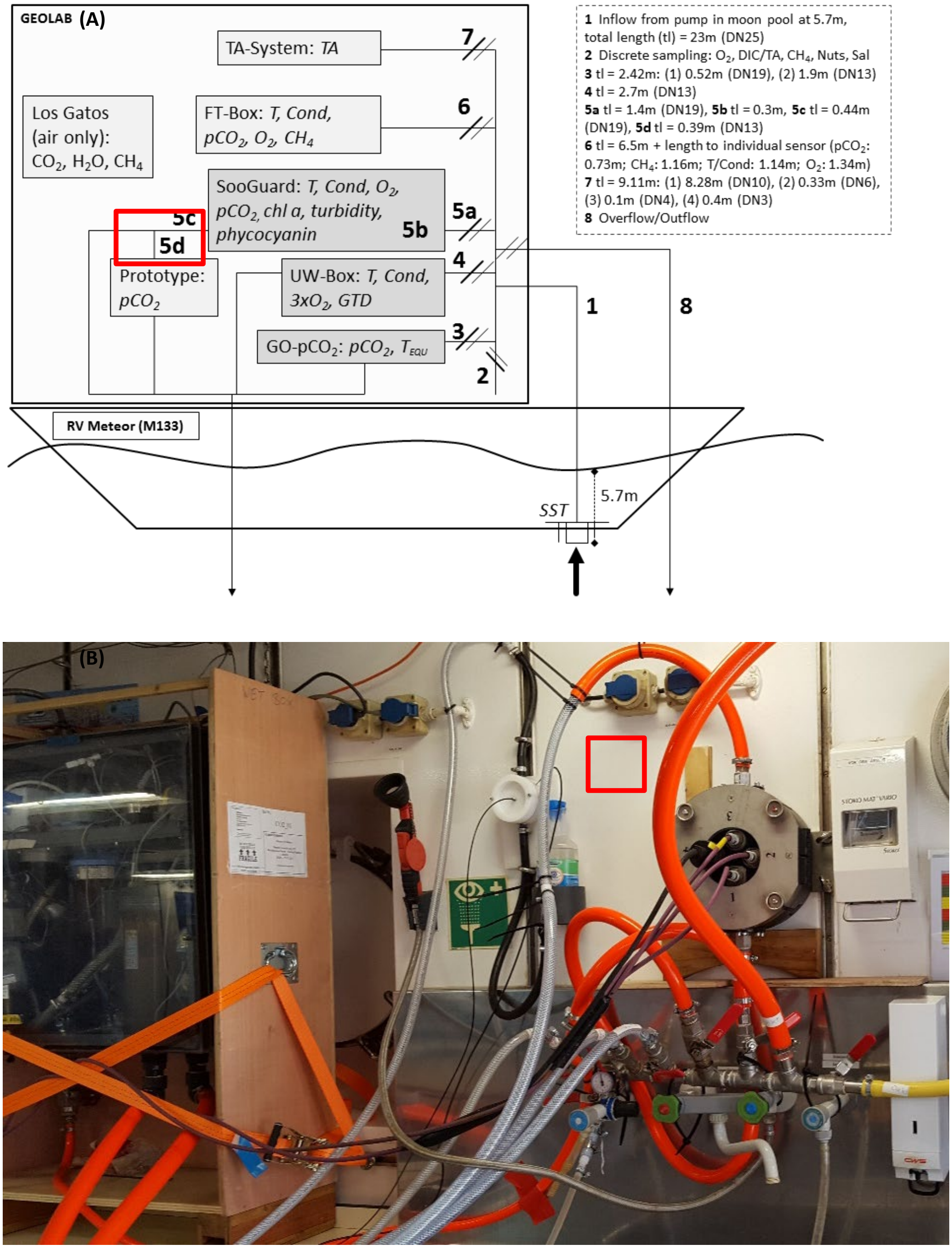


Figure 6: *(A) Schematic overview of all underway measurements carried out during the research cruise M133 of R/V Meteor. The CONTROS pCO2 prototype (flow line 5d, red box) was arranged directly behind optical pCO2 measurements from an Aanderaa pCO2 optode (model 4797). (B) Arrangement of the pCO2-GO-system (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 *p*CO_2 optode sensor (see Fig. 7.A) as well as the CONTROS prototype of a planar *p*CO_2 mini sensor spot optode (not shown here) did not provide useful data as compared to the reference GO underway *p*CO_2 system (see Fig. 7.B). After a trans- Atlantic section along 34.5°S (departure from Cape Town/South Africa) with relative stable *p*CO_2 in the 370-410 µatm, a generally lower and more variable *p*CO_2 of 220-360 µatm was encountered on the Patagonian Shelf from Jan 4th onwards. The Aanderaa *p*CO_2 optode does detects *p*CO_2 features qualitatively, particularly towards the end of the cruise. However, the *p*CO_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.

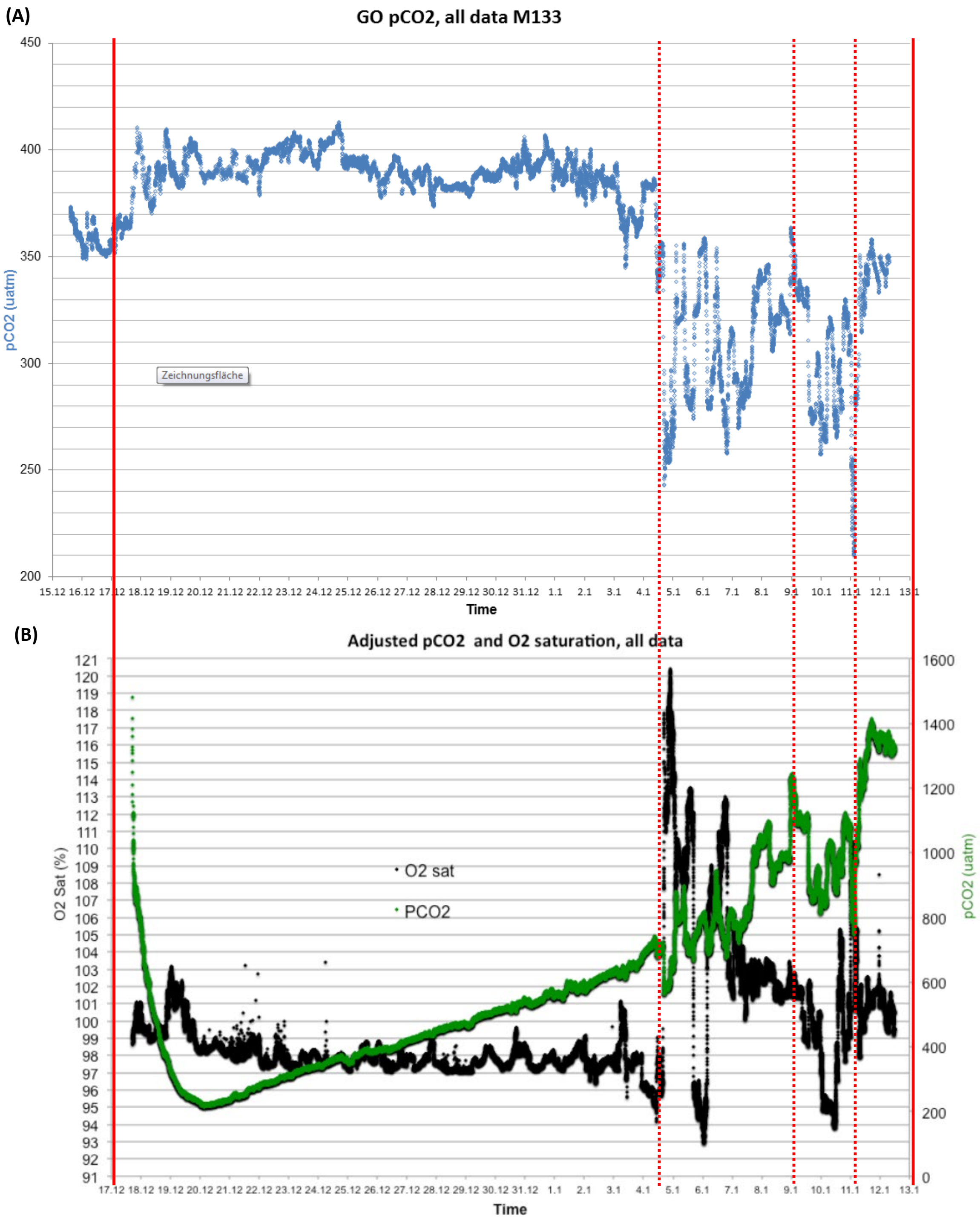


Figure 7. *Reference pCO_2 data from the GO underway pCO_2 system (A) and the Aanderaa pCO_2 optode (B, green symbols) as recorded between 15.12.2016 and 13.1.2017 over the course of the M133 cruise of R/V Meteor. After a trans-South Atlantic section along 34.5°S (departure from Cape Town/South Africa), data were recorded over the Patagonian Shelf from Jan 4th onwards.*

The development of a prototype of the KM CONTROS pCO_2 optode has been delayed then stopped, as the sensor's development was postponed by manufacturer due to other company priorities. We have continuously discussed this matter with the manufacturer, but no solution according with the ENVRIplus project timeline could be found. We therefore had to adapt the work plan as follows.

During the R/V METEOR Cruise M133 (15.12.2016 - 06.01.2017, Cape Town/South Africa to Port Stanley, Falkland Islands/UK), a multi-sensor pCO_2 intercomparison exercise has be carried out that has featured at least the following pCO_2 and other instruments/measurements:

- General Oceanics 8050 pCO_2 Measuring System (reference system);
- KM CONTROS HydroC pCO_2 sensor (submersible type);
- KM CONTROS HydroC FT pCO_2 sensor (flow-through type);
- KM CONTROS HydroFlash prototype pCO_2 optode;
- Aanderaa pCO_2 optode in SooGuard flow-through cell;
- KM CONTROS HydroFIA TA system (2^{nd} CO_2 system parameter);
- + discrete sampling for DIC/TA (2^{nd} and 3^{rd} CO_2 system parameter);
- KM CONTROS HydroFlash O_2 sensor;
- KM CONTROS HydroC CH_4 sensor;

All of these sensors intended to be operated throughout the cruise in autonomous flow-through or submerged (flow-through box) mode on the same water flow provided by means of a submersible pump installed in the ship's moon pool.

Results are exposed here after:

GEOMAR Continuous Alkalinity measurements during Meteor cruise M133 (extracted from cruise report)

- Successful operation of a HydroFIA TA analyzer during the research cruise M133 on RV Meteor from Cape Town, South Africa to Stanley, Falkland Islands, during 15.12.2016 - 13.01.2017
- Continuous underway seawater measurements at a 7 min interval and several experiments to gain insights into the behavior of the system under continuous measurement conditions (short term precision: 1.45 µmol/kg (mean out of 20 standard deviations), long term precision: 2.44 µmol/kg, run-in period after Milli-Q-Flush)
- Overall 3358 TA determinations were carried out (2702 were underway seawater measurements)
- Plans for the next 6 months:
- Discrete reference samples taken during the cruise and relevant for an accuracy assessment are still in transit back to Kiel. Their arrival is scheduled for April and the analysis for May-June 2017.
- Purification of the indicator Bromocresol Green, which is used during the TA measurements, and evaluation of its effect on the measurement performance.
- Further laboratory experiments (i.e. variation of the measuring temperature inside of the system)

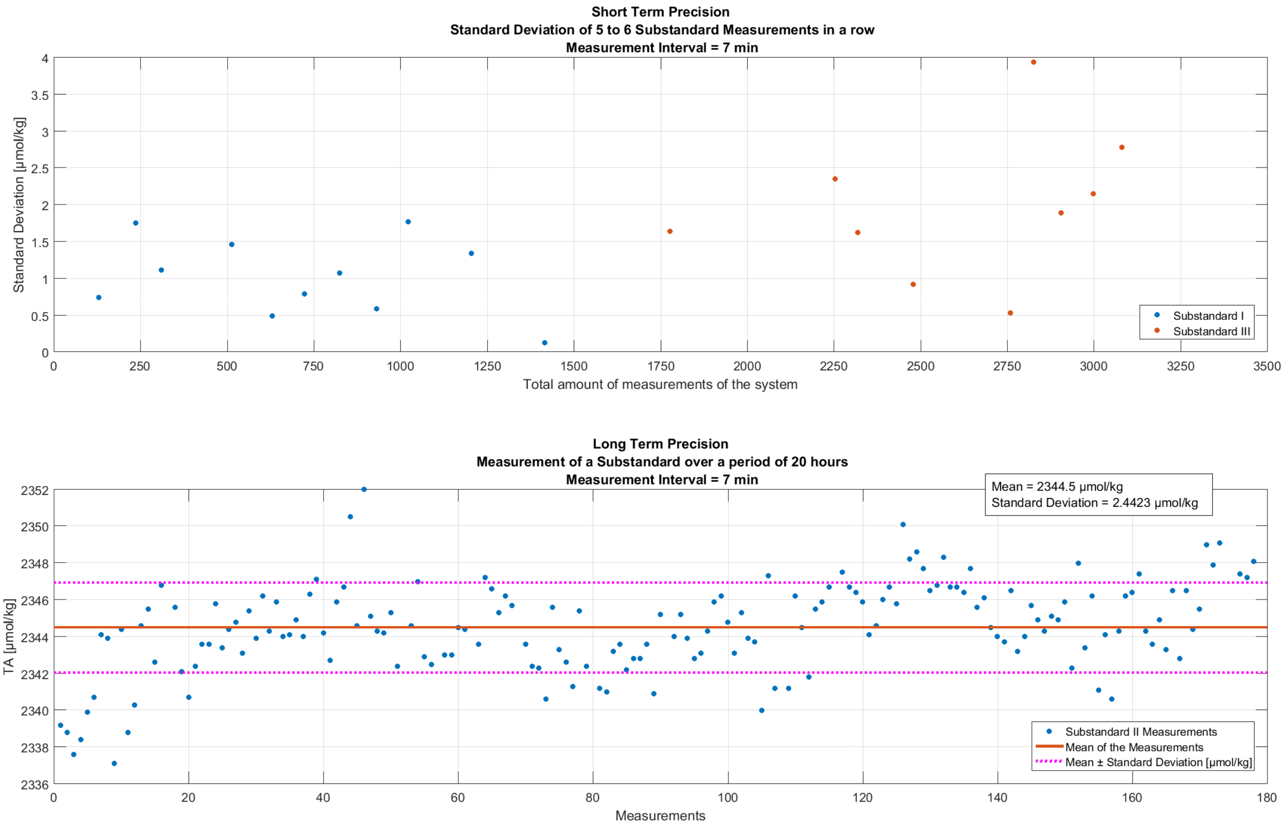


Figure 8. *Short Term and Long Term Precision of the KM CONTROS HydroFIA TA system (Cruise M133)*

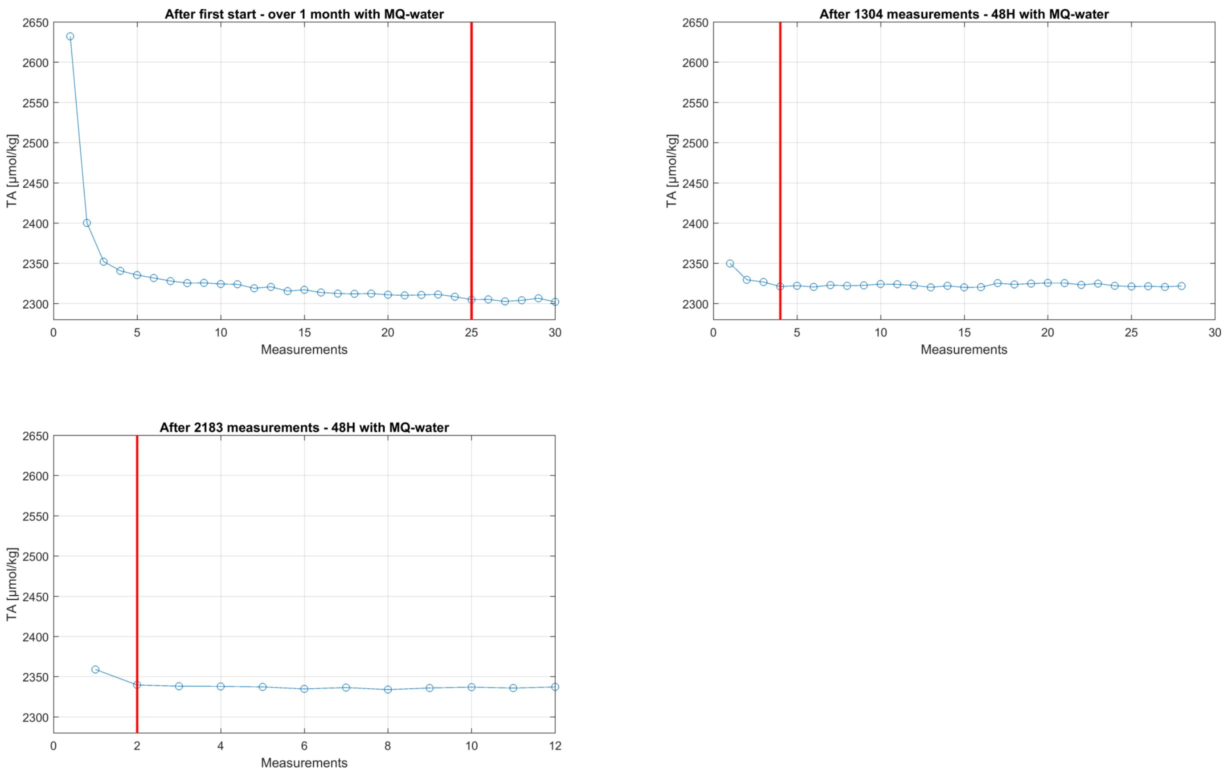


Figure 9. *Behaviour of the drift after MQ-Flush of the system (measurements after red vertical line = stable (Std-Dev. < 2 µmol/kg))*

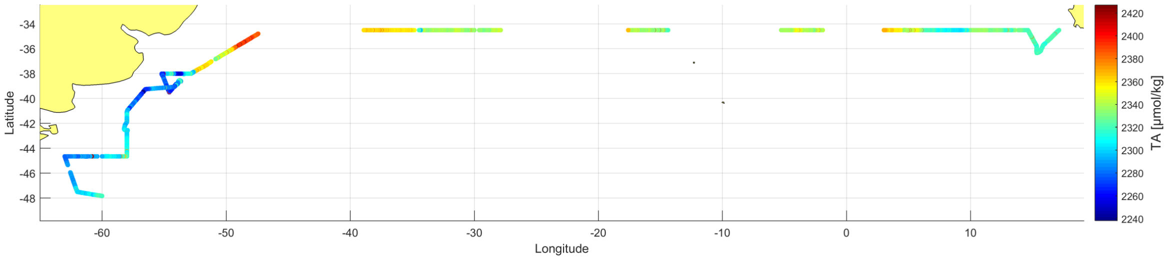


Figure 10. *Total Alkalinity of the underway seawater measurements over the Cruise Track (Gaps = Experiments were carried out)*

EUROARGO prototype profiling Float with pCO_2 deployment

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.

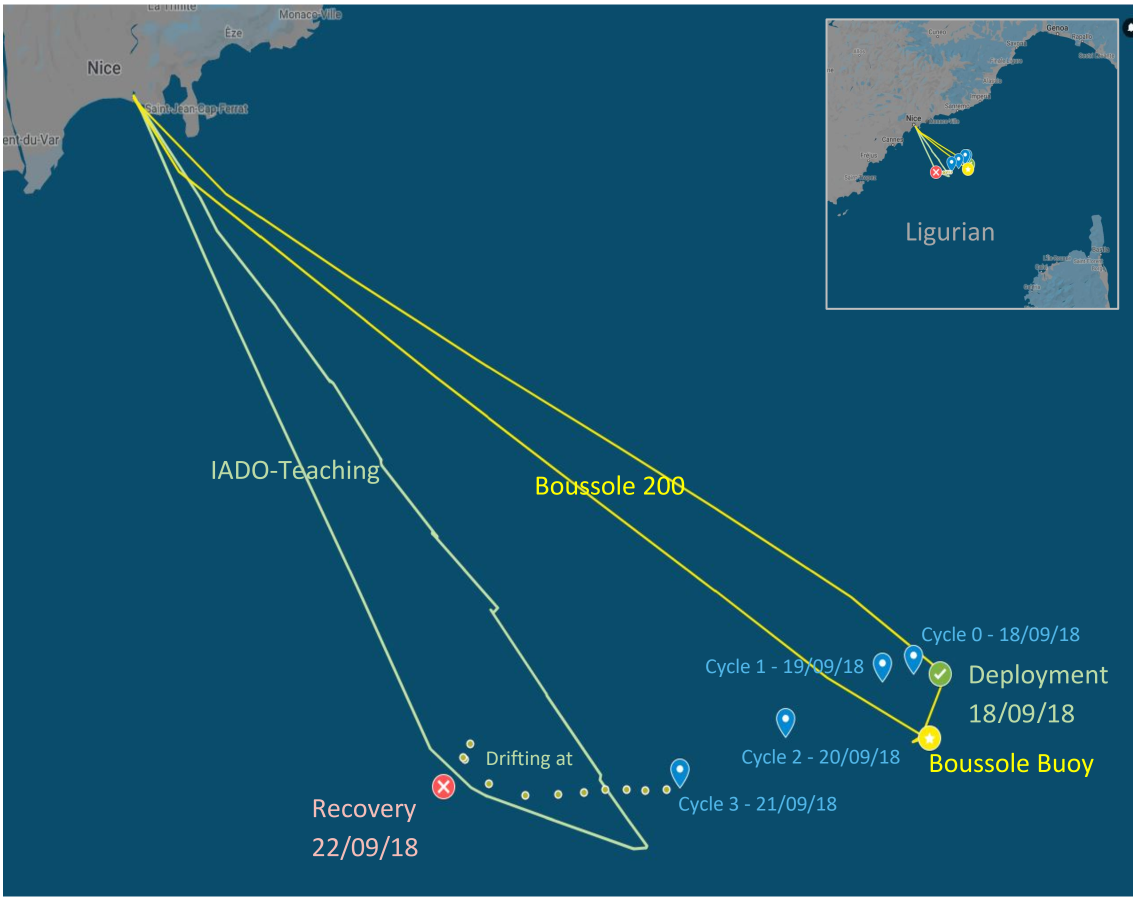
The DYFAMED/BOUSSOLE site presents all the features requested for a short-term deployment of a prototyped profiling float. Although located at 5 hours of ship time from the LOV premises, the water depth is about 2500 meters allowing a nominal profiling scheme to be programmed. The BOUSSOLE Buoy is equipped with a continuous sampling system for all the Physical and Bio- Optical parameters at surface, including a CARIOCA (SU/CNRS/NKE Instrumentations) sensor measuring pCO_2 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:

Deployment of the profiling float at BOUSSOLE site in Ligurian Sea

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.



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, providing 4 descending profiles during which pCO_2 sensor was ON, and 4 ascending continuous profiles Argo compliant but with pCO_2 sensor OFF.

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

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 pCO_2 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 pCO_2 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.

A new dedicated cruise is scheduled for summer 2019 in the Iroise Sea (Off-coast of French Brittany) from a sailing ship equipped with a reference underway pCO_2 analyser to better assess the scientific use of the float's pCO_2 produced dataset.

CONCLUSIONS

The measurement of the pCO_2 concentration is extremely challenging in the ocean and in particular at depth. The available equipment from the world market does not fulfill the requirements of all observing networks: Some sensors are dedicated to ship-borne implementation, some are suitable for moorings, and no one is fully compatible with long term autonomous platforms observing networks.

Multiple individual Initiatives have been carried-out by individual European environmental Research Infrastructures or oceanographic institutes to test and adapt the available technologies to specific platforms; the results are encouraging showing that the TRL of the sensors is increasing, but efforts of manufacturers to improve their equipment remains at a low stage since the final outlet is rather small.

The European Marine Research infrastructures have to maintain their efforts for collaborating in a common way for a complete inter-network approach.

ENVRIplus project demonstrated that this activity is extremely valuable at the European scale, and that synergies which have been developed during the project timeline have to be encouraged and further reinforced.