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# Technological Handbook and Assessment Report on CO2-ASV

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Public Document

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- Appearance is generally appealing and according to the RINGO template. Cover page has been updated according to the Deliverable details. ☐
- The executive summary is provided giving a short and to the point description of the deliverable. ☐
- All abbreviations are explained in a separate list. ☐
- All references are listed in a concise list. ☐
- The deliverable clearly identifies all contributions from partners and justifies the resources used. ☐
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## EXECUTIVE SUMMARY

Major uncertainties in marine and freshwater CO2 uptake/release occur because of the sparseness of observations, especially in locations remote from shipping routes or from laboratories where marine observations are made. Such locations include large ocean regions such as the Arctic and Southern Oceans, but also most rivers, estuaries and large lakes, and some near-shore coastal ocean environments which are not crossed by major shipping routes. One approach to address this problem is the development of instruments for surface water $pCO_2$ that can be mounted on autonomous surface vessels (ASVs) that can be deployed in these regions. We report here on the development of one such instrument, the "$CO_2$-ASV", in Task 3.3 of RINGO.

The instrument design and performance, as optimized for use on ASVs is described. For these platforms low power consumption, ruggedness and small volume were prioritized. High precision and accuracy of ±2µatm, specified by SOCAT for the highest quality data, (www.socat.info) was also specified for the measurements, so as to be of most use in quantifying $CO_2$ fluxes to or from the atmosphere. Laboratory and initial field tests showing the performance of the instrument are detailed, and indicate that the instrument meets these requirements.

The final stage of the task was to be a field testing mounted on an ASV, and extensive preparatory effort was put into this goal. However, COVID-19 restrictions have frustrated us and meant we have been unable to perform this field trial before the end of the project. As part of ICOS Ocean Thematic Centre-sponsored activities, in 2019 and 2020 we have been involved in a project utilizing a "Saildrone" ASV equipped with a NOAA-designed $pCO_2$ system, with a successful seven-month transit through in the Eastern North Atlantic and Western Mediterranean. Though not formally part of RINGO, we show some of those results to illustrate the potential of the $CO_2$-ASV approach for obtaining observations enabling air-sea fluxes to be quantified over substantial regions.

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# 1 INTRODUCTION

Much of the knowledge we have about the flux of carbon dioxide ($CO_2$) between the oceans and atmosphere comes from observations of surface water carbon properties, especially the partial pressure of $CO_2$ ($pCO_2$) (Takahashi et al. 2009). This quantity can be used together with knowledge of the atmospheric $CO_2$ partial pressure, and estimates of the gas transfer rate, to calculate the flux to or from the atmosphere. A substantial body of observations of surface $pCO_2$ have been made over many regions of the world ocean (Bakker et al. 2016), where the majority of such measurements have come from instruments mounted on fixed buoys, on research vessels and especially automated instruments on commercial vessels(Cooper et al. 1998).

However, major uncertainties in marine and freshwater CO2 uptake/release occur because of the sparseness of observations in locations remote from shipping routes or from laboratories where marine observations are made. Such locations include large ocean regions such as the Arctic and Southern Oceans, but also most rivers, estuaries and large lakes, and some near-shore coastal ocean environments which are not crossed by major shipping routes.

To address these uncertainties, there are now efforts to develop instruments that can be mounted on autonomous platforms such as ASVs that can reach such locations (Sabine et al. 2020). In contrast to conventional instruments mounted on ships or large buoys, where they are well-protected from the sea and with ample power available, instruments for use on ASVs need to be physically compact, rugged and waterproof, with low power requirements (Sabine et al. 2020). However, the accuracy requirements are no less strict than for conventional instruments: SOCAT specifies an accuracy of ±2µatm for the highest quality of observations required for open-ocean observations of $pCO_2$.

A number of instruments are now commercially available that are suited in some respects to mounting on ASVs and similar platforms, however maintaining this high accuracy over long deployment periods is problematic. Conventional instruments maintain this accuracy by use of gas standards contained in compressed gas cylinders – two or more standards at different $CO_2$ concentrations spanning the measured range are recommended - but commercially available designs for autonomous platforms do not include such calibration standards. A particular feature of our design is that it does include on-board calibration using multiple gas standards contained in very small high-pressure cylinders, which together with a low-dead-volume gas transfer pathway, enables periodic on-board calibration within the confines of a small and low-power-drain unit.

# 2. ROLES OF THE PARTICIPANTS, RESOURCES AND TIMELINE

The instruments were designed and built at the University of Exeter (UoE), with support from the NERC National Oceanography Centre (NERC) at Southampton in the UK. UoE is a "third party" under the RINGO contract, attached to NERC.

Eight months of time for junior scientist/senior technician level were charged to RINGO for this work, and expenditure on materials and consumables of 19000 euros for the construction and testing of the instruments, for travel and subsistence 1000 euros. The full cost of the work was substantially higher than this, with the difference being met by University and UK national funding.

The Timeline for this project was originally to design and build prototypes, conduct initial testing and begin integration into a vessel during the first 18 months, leaving months, leaving 18 months of iteration with further field trials as necessary, leading to completion of a deliverable report at month 36. This schedule had to be revised because we were unable to access the ASVs on this time scale, as described below in section 5, “Problems encountered”. The timeline as actually achieved was as follows:

| Period | Activity |
|---|---|
| January 2017 | Start of project – draft designs already available. |
| January-December 2017 | Design of gas and water valving, electronics, initial laboratory tests, target ASV identified |
| January – June 2018 | Revisions and iterations to design |
| July-December 2018 | Construction of generation 2 instrument with integrated electronics and valving: Slippage of goals as unable to obtain access to ASV |
| January-December 2019: | Laboratory tests, tests in local river, revision of design. Revision of components to fit new target ASV with tests planned summer 2020 |
| January – mid-March 2020 | Discussion with Plymouth Marine Laboratory – first test on *Plymouth Quest* |
| Late March-August 2020 | Laboratories closed, field work postponed and personnel on furlough due to Covid-19 lockdown |
| September 2020 | Recommence field tests on PML vessel. |

## 3. DESCRIPTION OF THE $CO_2$-ASV INSTRUMENT

Figure 1 shows a block diagram of the instrument, which for the most part is patterned after that of conventional ship-mounted $pCO_2$ instruments, but with components miniaturized when possible. It is designed to measure the $CO_2$ concentration in air, and in gas equilibrated with surface water, and in a series of calibration gases, where the software can be programmed to determine the sequence in which this is done. The $CO_2$ detector used is the a de-cased and configured LI-COR 850 $CO_2/H_2O$ gas analyser, chosen because it is a well-trusted and robust non-dispersive infra-red absorption-based analyser that has both $CO_2$ and $H_2O$ measurement channels, allowing for monitoring of the drying efficiency of the instrument. It also contains pressure and temperature sensors to measure the conditions in the cell. This is mounted in a core unit with additional electronics to control switching of gas streams, and collect and store data (figure 2 shows the core unit in and out of its casing). A detailed manual for the Li-Cor $CO_2$ detector is available on the web (https://www.licor.com/documents/y10gor2jal2p3t8ev4hm).

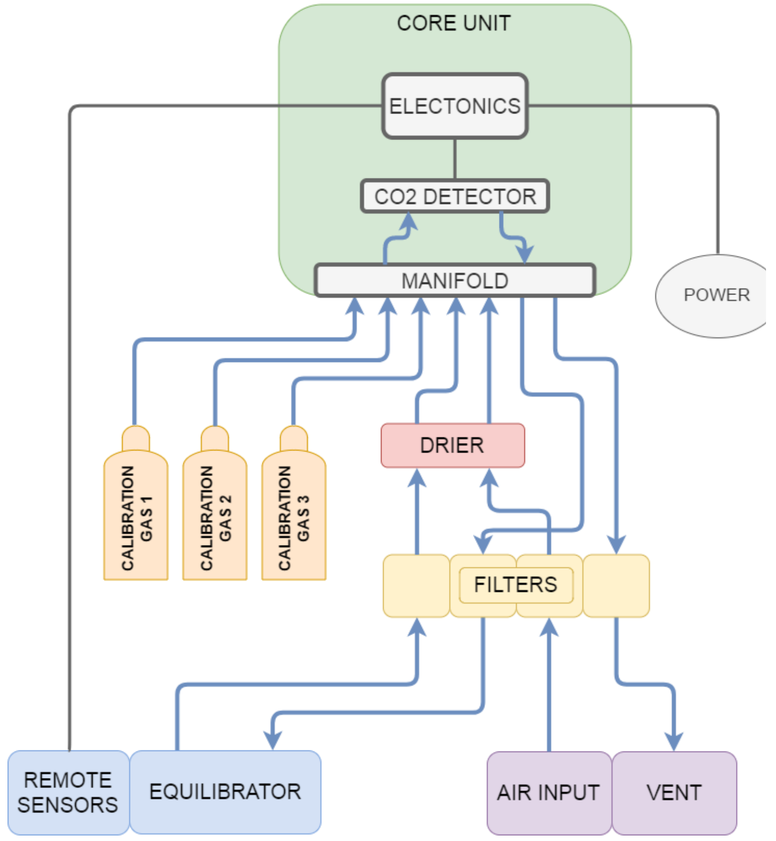



Figure 1: Block diagram of the instrument

Calibration: the instrument incorporates up to 3 calibration gases contained in miniature high pressure cylinders, each able to contain up to 40 litres of gas at STP. The concentrations of $CO_2$ in the calibration gases should be chosen to bracket the expected range of measurements, which in the open ocean will normally be in the range 250-550 ppm, but in estuaries, rivers and inland waters might be substantially larger. The LI-COR sensor incorporates linearization algorithms that can provide a signal that is much more linearly related to concentration than is the raw absorption signal. However, even when using this as the primary output, the highest accuracy is best obtained with 3 calibration points.

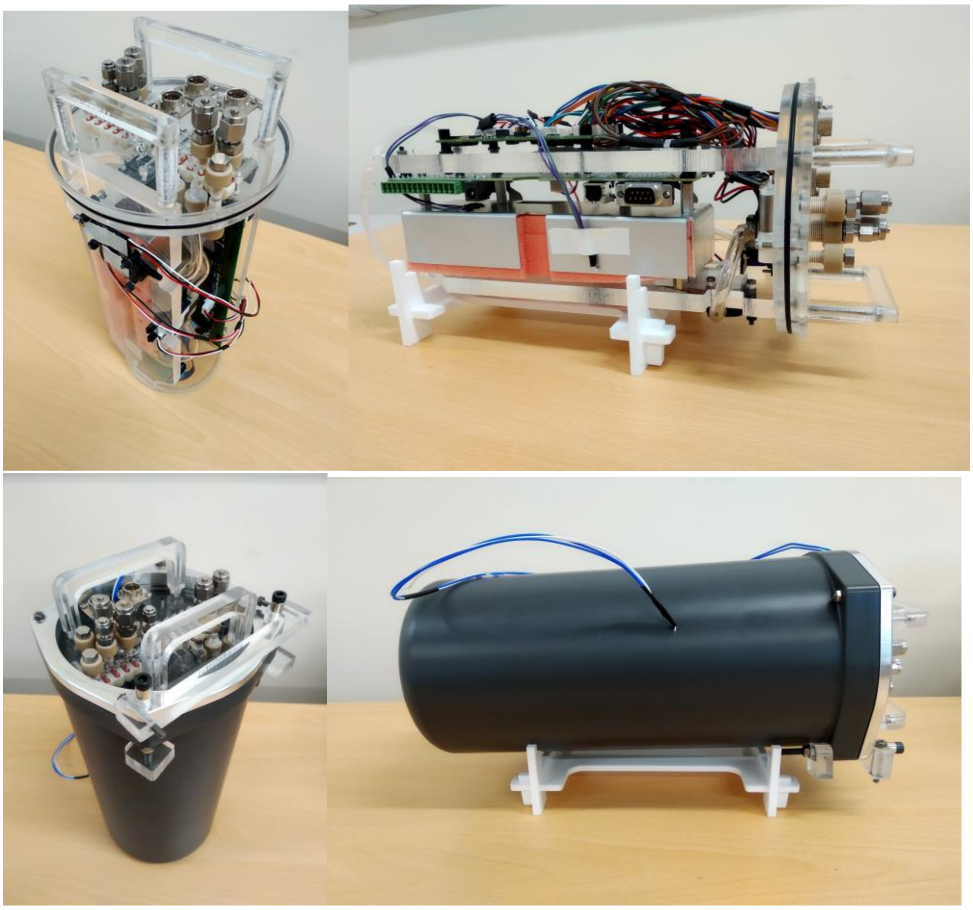


Figure 2: Core unit, removed from case (top) and inside case (bottom)

Equilibrator: the instrument incorporates a small equilibrator (Figure 3). This uses the design of the "h-shape" equilibrator (Sutton et al. 2014). The detailed design of equilibrator will vary depending on the vessel to which it is to be fitted: the one shown in the photograph should be suitable for wave-glider style of ASV with a low and constant freeboard: the h-style equilibrator needs no pumps to circulate the water through it, but works efficiently only if mounted so that the level of the sea surface remains within narrow limits.

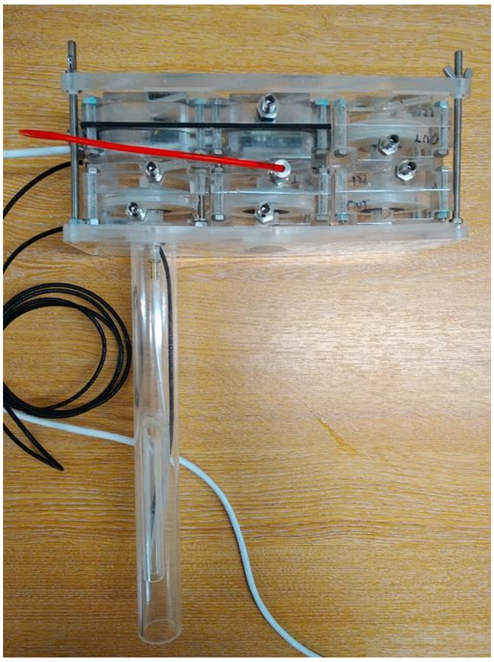


Figure 3: "h-shaped" equilibrator for wave glider

Drier: a drier consisting of a Nafion tube packed into a dessiccant material dries the gas flow. The drier is designed to have sufficient capacity to enable extended missions lasting several months.

Manifold: the valve switching manifold consists of 12 miniature latching valves that direct the gas flow from calibration gases, to and from the equilibrator or to and from air inputs and vents and are switched by the control software.

Overall configuration: This can be altered to fit the available space on the vessel to which it will be fitted. Figure 4 a, b, c shows the parts installed in the cargo-box of a wave-glider (a), and with the two halves of the cargo-box opened. In fig 4 b, the half of the box closest to camera contains the core unit, drier, control switches and pressure drop valve for the calibration gases. In fig 4c, the half of the box closest to camera contains the high-pressure cylinders and the filter unit. The equilibrator is mounted externally to the cargo box.

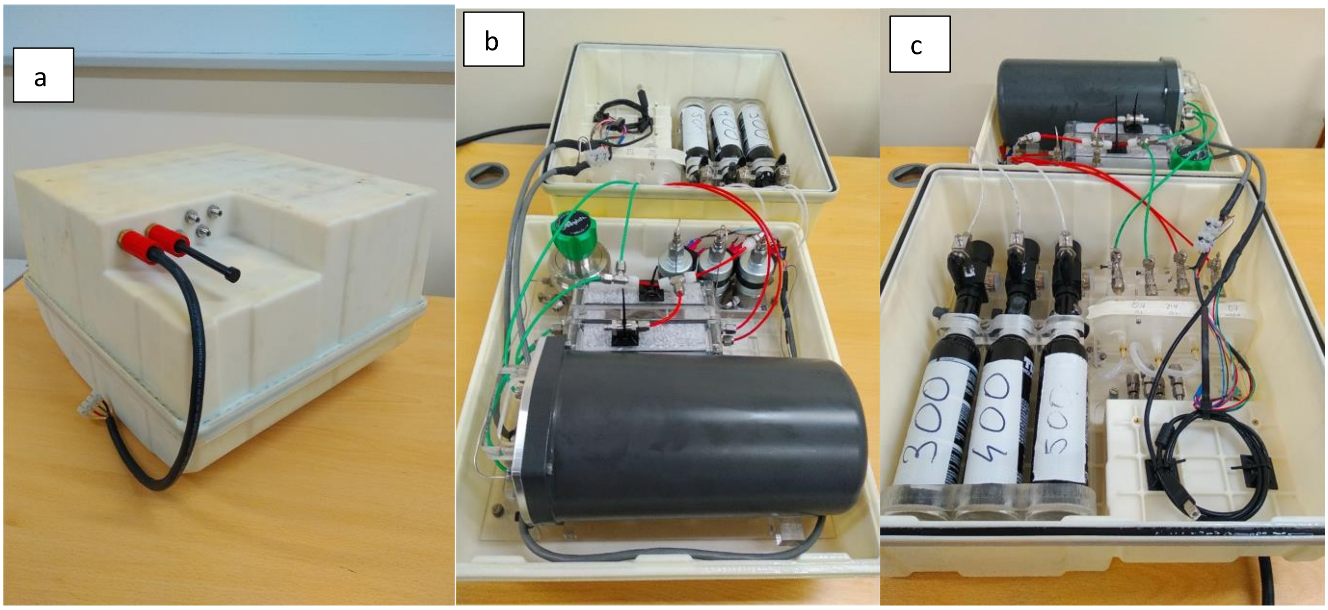



Figure 4: The instrument configured for waveglider: (a) assembled cargo box, (b, c) two views of the opened cargo box.

## 4. PERFORMANCE AND TESTS

Laboratory tests of precision and accuracy: The instrument has been tested in the laboratory, and verified that the precision of the $CO_2$ sensor and the associated gas circuitry is better than 1ppm $CO_2$ in dry gas for 1 second averages. In overall tests of accuracy to test gases, when calibrated with 3 standards at 300, 400 and 500 ppm the accuracy was <2 ppm. These tests do not fully evaluate the performance of the instrument since that is also dependent on the performance of the equilibrator and drier.

Laboratory response time tests: The response time of the instrument including equilibrator was tested by connecting to a tank of seawater in the laboratory, with the $pCO_2$ of the water then manipulated by addition of alkali and acid to the water (figure 5). The response of the equilibrator was typically in seconds after addition of base/acid, depending on the flow rate of gas through the equilibrator and water mixing in the reservoir.

Power consumption: while making measurements the power drain of the instrument is approximately 3.5 watts. However, the software has a low-power standby mode, and when used for long deployments on platforms where power is limited, the instrument could spend much of its time in this mode, trading frequency of measurements for reduced power consumption so that its overall power needs stay well within the capabilities of the platform by trading off measurement frequency against power consumption. Most ASVs for example, carry solar PV panels to generate power.

Tests at sea: We have been able to run preliminary tests of the instrument on board the *R/V Plymouth Quest*, a small research vessel operated by PML, who have kindly allowed us access. At the time of writing only two trial-days have been possible, due to a combination of Covid disruption (from March-August and again from October this year) and weather delays. We do however .

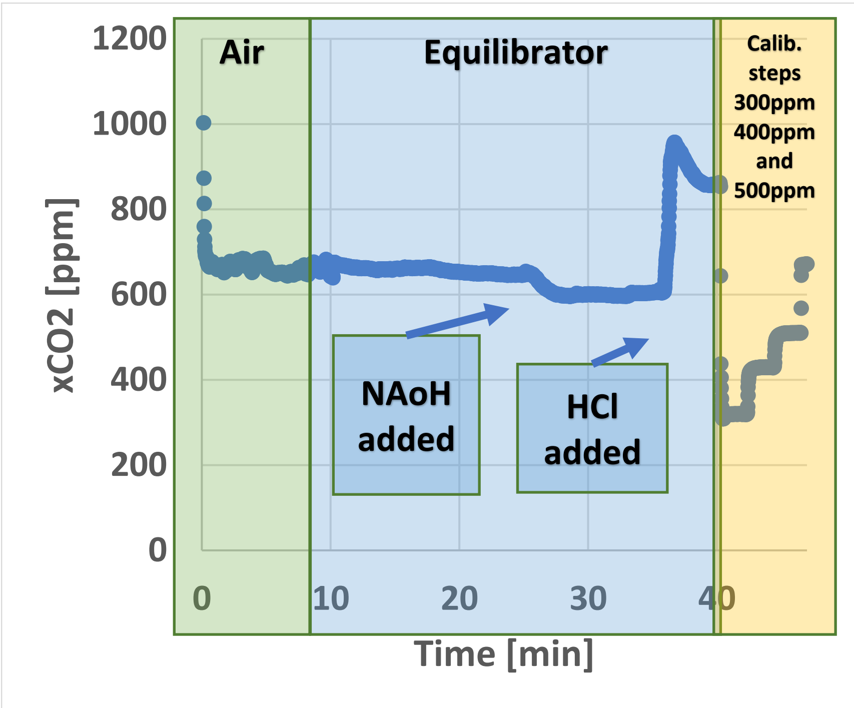



Figure 5: response of the instrument including equilibrator to change in the $pCO_2$ of test seawater by additon of alkali and acid.

## 5. PROBLEMS ENCOUNTERED

**1. Availability of ASV**: At the start of the project we planned the use of the "Autonaut" ASV (see https://www.autonautusv.com/ ) owned by NERC and held at NOC Southampton. It became apparent about a year into the project that this would be an unwise choice, as the vessel proved not adequately seaworthy in trials carried out by NOC, being subject to leakage through the seals of the hatches covering the spaces in the hull for payloads, with potential serious damage to, or loss of, the instrument. The vessel owned by NOC was the first that the manufacturers delivered. We are told that this defect has subsequently been remedied, but it proved unfixable on this prototype.

Through the period 2018 – 2019, we had repeated negotiations with NERC at NOC Southampton, in an attempt to get access to ASVs for a long enough period to conduct out tests. Several solutions were proposed, including initially a "C-Worker 4", a large diesel powered ASV which in 2018 was earmarked for our use, but which was later withdrawn. Eventually, we were able to negotiate with NOC the use of another ASV, a Liquid Robotics "wave-glider" (https://www.liquid-robotics.com/wave-glider/how-it-works/) for our trials. This entailed however a substantial re-design of the $CO_2$-ASV instrument to fit into a smaller volume, since the volume available in the body of the wave-glider is much more limited than in either the Autonaut or C-worker vessels. Our trials with the wave-glider were scheduled for Summer 2020 in Scotland. In the meantime we were able to run some tests using makeshift and temporary platforms in the River Exe, and with help from Plymouth Marine Laboratory we have made initial tests of the instrumentation on their vessel, the *R/V Plymouth Quest.*

**2. Covid-19 disruption**. From mid-March 2020 all laboratory and field work ceased until mid-August. Field work again ceased from October 2020 to the present. Our trials using the wave-glider were cancelled and are not now scheduled until March 2021. We are unfortunately unable therefore to report on the results of these trials in the RINGO project.

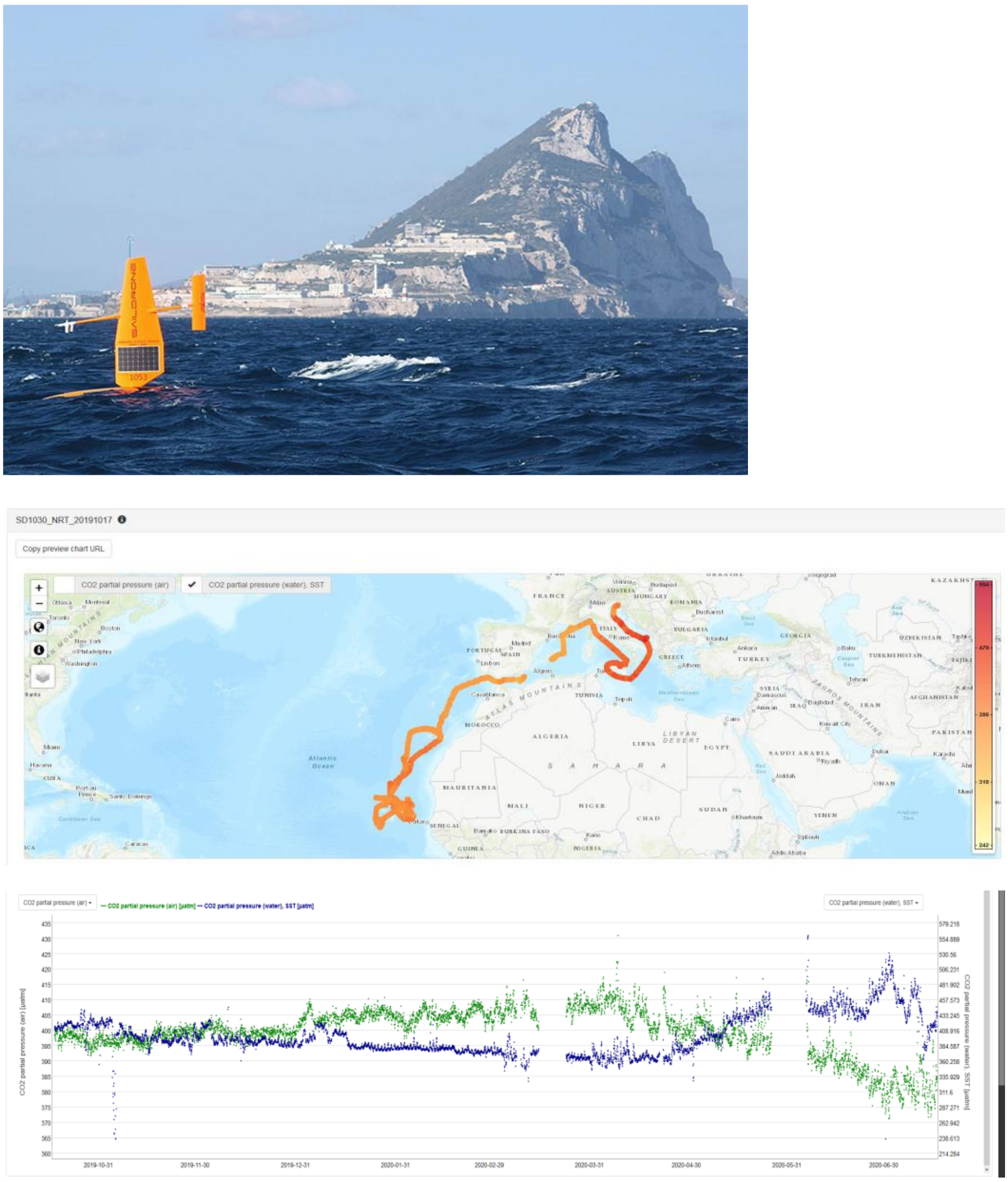
## 6. ATL2MED: AN ILLUSTRATION OF THE POTENTIAL OF ASVS FOR $CO_2$ OBSERVATION

Though the work with our instrument has progressed more slowly than planned, within ICOS Ocean Thmatic Centre we have simultaneously been involved in a project using a US "Saildrone" ASV (www.saildrone.com), equipped with a $pCO_2$ instrument built by NOAA colleagues at the Pacific Marine Environmental Laboratories in Seattle. This instrument is not commercially available, but was developed by

PMEL from the design of "MapCO2" instrument design that has been in use for more than 20 years by their laboratory, originally for use on large fixed buoys. To our knowledge, it is the only other ASV-compatible instrument besides our own that incorporates a calibration gas, and which therefore meets the demanding specifications required by SOCAT for the highest quality of open ocean observations.

ATL2MED ran for more than seven months, for most of which time the vessel was at sea. It served the useful purpose of validating a number of fixed ocean carbon observing stations in the Eastern Atlantic and in Mediterranean, while also providing valuable transit data. The data are available via the Carbon Portal. We include it in this deliverable to demonstrate the tremendous potential of ASVs equipped with $pCO_2$ instruments to assist in building a more complete and reliable understanding of the ocean sink/source of $CO_2$ with respect to the atmosphere.

Figure 6, ATL2MED: Saildrone off Gibraltar, the track of the seven-month mission , and the record of atmospheric (green) and surface water $pCO_2$ (bue) obtained. Note the different scales for the atmospheric and surface water traces.



# 7. CONCLUSIONS

1. The prototype $CO_2$-ASV instrument, developed and built during this project, is able to meet the critierion of an accuracy of ±2µatm for measurement of sea surface and atmospheric $pCO_2$, while having the small volume and low power consumption necessary for operation on ASV platforms.
2. All the stages of design and construction have been successfully executed except the final field tests on an ASV. These were delayed initially by the necessity to change our target ASV platform starting at around month 12. They were then scheduled for summer 2020 but were cancelled because of the Covid-19 pandemic.
3. In the absence of these sea-trials we cannot show data from our own instrument. However, the potential of ASVs for marine $CO_2$ work is illustrated by the ICOS – Saildrone ATL2MED project, which used an instrument built by NOAA-PMEL on board a Saildrone, for a seven-month mission from the Northeastern Atantic and Western Mediterranean in 2019-2020.

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## 9. DEFINITIONS, ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ASV | Autonomous Surface Vessel |
| ATL2MED | ICOS-OTC project with Saildrone, obtaining carbon observations in the Eastern North Atlantic and Western Mediterranean |
| $CO_2$: | Carbon dioxide |
| $CO_2$-ASV | The surface $pCO_2$ instrument developed in RINGO. |
| $pCO_2$ | Partial pressure of carbon dioxide in equilibrium with surface water |
| PMEL | Pacific Marine Environmental Laboratory (Seattle, Washington, USA) |
| PML | Plymouth Marine Laboratory |
| NOAA-PMEL | The Pacific Marine Environmental Laboratory of the US National Oceanic and Atmospheric Administration. |
| NOC | National Oceanography Centre, Southampton |
| SOCAT | The Surface Ocean $CO_2$ Atlas (www.socat.info) |
| STP | Standard Temperature and Pressure (0°C, 1013.25 mbar) |