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D3.3

Technological handbook and assessment report on implementation of ATC-conform atmospheric measurements of CO_2 (and CH_4) on SOOP lines

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Deliverable Review Checklist

A list of checkpoints has been created to be ticked off by the Task Leader before finalizing the deliverable. These checkpoints are incorporated into the deliverable template where the Task Leader must tick off the list.

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

EXECUTIVE SUMMARY

The ICOS Ocean observational program is running autonomous systems to measure the partial pressure of CO_2 (pCO_2) in surface waters on commercial carrier ships (Ships Of Opportunity, SOOPs). Atmospheric dry air mole fractions are measured less frequent or not on SOOP lines, and are usually not acquired according to standards required for high-quality atmospheric measurements. Improving the atmospheric part of the measurements on SOOP lines according to the WMO and ICOS-ATC guidelines has been identified as a potential cost-efficient way to to enhance/improve the geographic coverage of lower atmosphere and near surface ocean atmospheric measurement. RINGO Task 3.2 developed and tested technological solutions for three different settings and approaches.

We were able to install systems for ATC-conform measurements of CO_2, CH_4, and CO on two SOOPs (TAVASTLAND and COLIBRI) established within the OTC network of surface seawater pCO_2 measurements, which are characterized by very different modes of operation with respect to environmental conditions and round trip times. At the ATC, required solutions for the handling and processing of these specific data were implemented, including position-related data, individual handling of different areas such as harbours and open sea transects, and spike identification. Evaluation of target measurements so far confirm a quality of data matching ICOS criteria, and first consistency tests with nearby atmospheric stations of the ICOS network (TAVASTLAND) and the CAMS forecast (COLIBRI) appear promising. The latter, above all, demonstrates the potential value of the open ocean data to validate the CAMS product. On SOOP ATLANTIC SAIL, amendments to the established system for the determination of pCO_2 in the surface water were made in order to improve the sporadical (every 3h) measurement of atmospheric air, and resulted in a repeatability of ~0.1 ppm for air measurements in this "dual operation" mode. First tests of a new CEAS instrument suitable to replace the NDIR-instrument currently mostly used by the ocean community indicate the potential for further improvement.

This report consists of two main sections. A "Handbook" part with some general guidelines to be followed prior to and during installation of own systems or amendments of pCO_2 systems for atmospheric CO_2 and trace gas measurements, and an "Assessment" part with detailed information on the technical realization and first performance and quality assessment of the three setups realized within RINGO Task 3.2.

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1 INTRODUCTION AND MOTIVATION FOR THIS HANDBOOK

The ICOS Ocean observational program is running autonomous systems to measure the partial pressure of CO_2 (pCO_2) in surface waters on commercial carrier ships (Ships Of Opportunity, SOOPs), which allows for high spatiotemporal data coverage, and is a major component of the OTC data stream. Atmospheric dry air mole fractions are measured less frequently or not on SOOP lines, and are usually not acquired according to standards required for high-quality atmospheric measurements. Improving the atmospheric part of the measurements on SOOP lines according to the WMO and ICOS-ATC guidelines has been identified as a potential cost-efficient way to enhance the atmospheric data coverage and to gather data from areas difficult to access, in some cases at critical regions in terms of air mass boundaries.

Within RINGO Task 3.2, different technological solutions were developed and tested. This included the installation of independent continuous measurements of atmospheric CO_2, CH_4, and CO mole fractions on board of the SOOP line COLIBRI, which cruises from France (Le Havre or Marseille) to French Guiana (after stopover in Livorno, Italy, and/or St. Petersburg Russia, and on the SOOP TAVASTLAND, running between Lübeck, Germany and Oulu, Finland. Both ships are components of the oceanic component of ICOS with established measurements of pCO_2 and other marine biogeochemical parameters, which are recorded simultaneously to the atmospheric measurements, but on completely independent systems. The environmental boundary conditions of the two lines are quite different. SOOP COLIBRI has a long travel time, with relatively low repetition rate and covering an enormous range of climatic conditions from Europe to the tropics. In contrast, the track of SOOP TAVASTLAND is surrounded by the northern European landmasses around the Baltic Sea, and reaches almost to the Arctic Circle, with several months encountering temperatures below 0°C in the northern part. The round trip time of the vessel is one week, which allows for frequent maintenance and a more homogeneous data frequency.

A different approach was evaluated on the SOOP ATLANTIC SAIL commuting between Liverpool, United Kingdom, and Halifax, Canada, where an attempt was made to achieve non-continuous, but mostly ATC-conform atmospheric CO_2 data retrieval using the analytical instruments primary used for the measurement of seawater pCO_2 in a "dual use" mode. The major aim of this set up is to develop a solution with existing equipment to generate high quality atmospheric air measurements, though with a reduced spatiotemporal data coverage, at very low additional costs. An overview of some of the main characteristics of the three installations is given in Table 1.

This Deliverable Report consists of two strongly related components. The "Handbook" part should serve as a guideline for future installations of atmospheric measurements on SOOP lines within the ICOS framework. There is no "one and only" way to set up such a system, as for various parts, the solutions might be country-dependent when it comes to supply and manufacturers. Measurement systems working on a full atmospheric measurement setup should follow the newest version of the ATC specifications, thus the main focus in this deliverable is on installation-specific considerations on SOOPs, also with respect to postprocessing.

The second part of this document is a report on the technical realization, status, and assessment of the three installations, representing the progress made until the end of the RINGO project and giving some examples of early applications and quality assessment. All installations will remain operational at least in the near to mid-term future, which will allow further evaluation with respect to the usage and long-term value of the measurements.

Ship	SOOP TAVASTLAND	SOOP ATLANTIC SAIL	SOOP COLIBRI
Route	Baltic Sea; Lübeck - Oulu	North Atlantic; Liverpool - Halifax	Around Europe with several ports; across the Atlantic from Europe to French Guiana
Round Trip Time	One week	Five weeks	N/A in European coastal waters due to varying schedule; ~1 month for the round trip across the Atlantic
Instrumentation	Continuous ATC conform station based on Picarro G2401 analyser	Periodic measurements of atmospheric air using an NDIR sensor (Licor LI7000, LI6262) or a laser based system (Picarro or Licor LI7815)	Continuous ATC conform station based on Picarro G2401 analyser
Frequency of atmospheric measurements	Quasi continuous	Ca. 10 minutes every 3 hours	Quasi continuous
Rationale/Question	Transect surrounded by atm. network, continental to arctic air masses, large temperature gradient	Determination of the quality of atm. CO_2 measurements that can be reached using OTC-typical pCO_2 setup	Transect covering highly undersampled air masses with a large range of meteorological conditions (temperature, humidity …)

***Table 1**: Characteristics of the three installations for high quality atmospheric measurements on SOOPs realized within RINGO Task 3.2.*

2 HANDBOOK FOR TECHNICAL REALIZATION

This handbook should provide some general guidance for the installation of high-quality atmospheric trace gas measurements on SOOPs. This includes considerations prior to the decision and planning for the installation, an overview of a typical installation and the existing specifications and installation guidelines, as well as an short overview of post-processing steps and quality assurance.

2.1 Pre-installation considerations

2.1.1 Consideration of added value

Sporadic measurements of atmospheric CO_2 on Research Vessels or SOOPs have so far mostly been used as an additional quality control for the waterside pCO_2 measurements, or to better constrain the local air-sea disequilibrium of pCO_2 for in situ air-sea flux calculations. The resources for the installation of an own system for atmospheric trace gas measurements, and even the effort to maintain enhanced quality of atmospheric measurements using the existing instrumentation for water measurements (but still requiring additional calibration gases provided by the CAL as well as implementation in the ATC data processing structure), cannot be justified for this purpose alone. Rather, the installation must have a clear added value for the atmospheric network.

In order to evaluate beforehand whether data along a certain transect and with a certain sampling frequency would be of value to reduce uncertainties in CO_2 flux estimates, so-called observation system simulation experiments (OSSE) based on synthetic data (or pseudo-data) can be done. They start from a given space-time flux field ("known truth"), which is transported in an atmospheric transport model. From the thus-modelled atmospheric field, the pseudo-data are sampled at the same locations and with the same frequency as the real (existing or planned) measurements. Then, the pseudo-data are used to constrain the inverse estimation of fluxes. The level of agreement of this reconstructed flux field with the "known truth" depends on the information content of the assumed data set. The increase in agreement between an OSSE using the existing data only and an OSSE using both existing and planned data is a measure of the added value of the planned data given the already existing ones.

Alternatively, the concept of the "Reduction of Uncertainty" (RoU) can be used. The a-posteriori uncertainty of an inversion does not depend on the actual data values, but only on transport (including the locations and times of data sampling) and the assumed uncertainties for the prior and the model-data mismatch. Therefore, it can also be calculated before data are available. Similarly to the evaluation based on OSSEs, we can compare the a-posteriori uncertainty when using existing data only or when using both existing and planned data. The relative change in the uncertainty again quantifies the added value of the planned measurements.

Both methods are well-established in the atmospheric inversion community, and tend to give equivalent results. The OSSE method has the disadvantage that it somewhat depends on the particular "known truth" chosen, but on the other hand it is much more easy to implement. For both methods, one has to define the spatial and temporal scales for which the agreement or the RoU, respectively, are evaluated.

2.1.2 Communication with ATC /OTC/CAL and the respective MSAs

Installation or improvement of atmospheric measurements on a SOOP line are per definition bridging the realms of the atmospheric and oceanographic communities represented by the respective MSAs and the ATC and OTC, respectively. Addressing these entities before a planned installation is strongly recommended to make best use of the joined expertise of both fields. The ATC is definitely best suited to advise and provide contact information on the actual trace gas measurement, including the most recent documentation of ATC-conform specifications, potential experienced members of the MSA who could give advice on the realization of the trace gas measurement system, and site-specific considerations (e.g. sea spray inlet protection, condensation or freezing issues, see section 2.2.3). Also, the potential data flow based on the ship track could already be prepared by the ATC. The OTC and members of the ATC could give advice on available ships, including link to other networks of interest like Eurofleets or the Ferrybox-Network as part of EUROGOOS, as well as provide expertise and/or contacts concerning the aspects which are more application-specific, such as additional safety regulations and material suggestions with respect to e.g. corrosion, legal aspects concerning the data acquisition across national boundaries, etc. Lastly, measurements which should feed into the ICOS ATC network will inevitably need high quality standard gases, best provided by the CAL. Therefore, even in a case where the installation and maintenance could be realized without additional cost involvement from the different ICOS organizational bodies, the provision of calibration gases by the CAL should be discussed and initiated well before the beginning of the initial steps of realization.

2.1.3 Communication / Planning with the shipping company

Executing scientific measurements on a SOOP line requires a frictionless collaboration and well maintained relationships between the host (ie. the ship owner, ship operator and shipping company) and the guest (i.e. the scientists and technicians involved in the installation). In fact, the relation between shipping companies and “science” has been identified as a very important point and potential bottleneck for the ocean community, and “ship liaison and network design” is an objective on its own in the working portfolio of the ICOS OTC. As there is usually no commercial added value for the shipping company other than that the hosting of environmental research might fit into the strategic environmental or public relation strategy, consideration of the shipping company’s interest is of utmost importance. Explaining the value of the measurements for society, envisioning a contribution to the company's customer journal or other public relation products, provision of meteo data can be incentives for the decision, but this might be very dependent on the function of the staff involved. Very often, the decision making bodies for a scientific installation are not located on the ship, so inquiring about the right “address” for information about a new installation or amendment is important. In most cases, once the decision is made, the captain and crew on the vessels are quite supportive despite the fact that they have no time contingent to assist with the installation or maintenance of the installation. As various issues concerning “ship liaison” arose during the project, we try to give an overview of aspects to be considered prior to and during the installation. In case no already established contact with the shipping company exists, we recommend to contact the ICOS OTC for advice.

Once the contact with the ship is made (new ship or just adding to an existing installation) one should prepare the following documents:

- <u>Technical drawing</u>: This drawing doesn’t need to be too detailed for the internal installation. But one needs to point out very detailed any possible hazardous parts (pressure cylinders,...) and needed connections from the ship’s side (power, GPS, network, water);
- <u>Dimensions</u>: The space exactly needed needs to be specified. Space is an issue on most ships, and therefore has to be outlined with high accuracy;
- <u>List of used materials</u>: specific regulations might exist for materials on ships, in particular concerning fire safety class; this might lead to the exclusion of some components which would not be problematic on a land-based ATC installation;
- <u>Installation effort</u>: A list describing what is needed from the ship’s side for installation (welding, power connections, potentially cut outs for air tubes, GPS antenna cable etc.;
- <u>Maintenance effort</u>: A list describing what routinely maintenance is expected by the crew (daily/weekly leak check turn on/off,...); it is encouraged to foresee a degree of automatization to minimize this effort.

2.2 Technical realization

In this chapter, an overview of the main technical characteristics of the installation for atmospheric measurements on SOOPs is given. Chapter 2.2.1 addresses the installation of own independent instrumentation for continuous measurements using an ATC-conform setup (like on SOOP TAVASTLAND and COLIBRI), while Chapter 2.2.2 deals with the solutions for (non-continuous) high-quality atmospheric measurements using a classical seawater pCO_2 measurement setup.

2.2.1 Systems with own instrumentation for atmospheric measurements

2.2.1.1 Trace gas system following ATC guidelines

<u>Using ICOS ATC documentation</u>

In order to assure the highest level of accuracy in atmospheric trace gas measurements, ICOS atmospheric stations follow very strict specifications and for various of the vital parts, allow only a very limited number of instruments (e.g. list of sensors allowed for the actual air measurements; gas regulators and gas pipe materials, meteo sensors, gas drying equipment, etc.). It has to be emphasized that the sensors used have to be run through a thorough performance check at the ATC prior to installation. Based on raw data delivered to the ATC, the postprocessing is performed here and the data are then accessible by the station PI for further QC. This is another reason why only the continuous gas analyzers approved by the ATC can be used. It is recommended to familiarize with the ATC homepage and in particular visit the documentation website

https://icos-atc.lsce.ipsl.fr/d

where the most recent version of the ICOS atmospheric specifications are publicly available.

At the time of the finalization of this report, this is the ICOS Atmosphere Station Specifications 2.0, launched in September 2020 (ICOS RI, 2020). This monograph contains all information about specifications and brands of ATC approved components, as well as important recommendations on the set up and installation.

The application on a SOOP line put further constraints on the installation. Evidently, some of the location recommendations do not apply. SOOP lines follow tracks, so providing measurements from a suite of locations, yet at the price of rare visit of any individual position along the track. Additionally, the inlet system is inevitably in very close distance to a major anthropogenic point source, i.e. the vessel itself. Consideration of the best position of the gas inlet on the ship is therefore of utmost importance. Still, frequent contamination signals in the data set will be the rule rather than the exception, in particular when the ship is heading with the wind (tail wind). For routine detection of contamination, the installation of a sensor detecting CO_2 and CO is therefore recommended (see Chapter 2.2.5 and El Yasidi et al., 2018). In case of the installations on SOOPs COLIBRI and TAVASTLAND, the Picarro G2401 was used.

In deviation from the situation on a platform on land, the measurement of wind velocity and direction has limitations. The installation height of the sensor will in most cases not be at the recommended height of 10m, which would also put the sensors at risk with respect to sea spray, icing, and in open ocean conditions even waves. Strictly speaking, waves and the ship's motion compromise the concept of a fixed height of the measurements. Moreover, the sensors could only derive true wind velocity and direction from the relative wind measurements on the ship, therefore speed and course over ground are essential variables for the calculation. Even when using sensors as specified by the ATC, it will not be possible to provide the required accuracy of the derived values of true winds as specified by the ATC. Still, the data can be the best measured data in that area of the open sea. Moreover, relative wind has the potential to be used as additional parameter for the contamination detection. Currently, this information is not implemented in the ATC data stream.

Additional important considerations specific for the installation on a SOOP line or any other ship are detailed in Section 2.2.3. A list of all major components used for the instrument build for SOOP TAVASTLAND is provided under Appendix A1.

2.2.1.2 Choice of calibration gas set up, calibration routine, and target measurements

Following ATC specifications, a set of three calibration gases and a target gas provided by the ICOS CAL with certified mole fractions for CO_2, CH_4 and CO was used on both SOOP COLIBRI and TAVASTLAND. Due to the temporal nature of the installation, no long-term target was provided for the installations at this stage. The concentration range was very similar in both cases and the values for the calibration and target gas used on SOOP COLIBRI is given in Table 2. Full calibration of the system following ATC-conform procedures should be performed about once per month. Details are given in the ICOS ATC station specifications (ICOS RI, 2020).

Cylinder ID	CO_2 (µmol/mol)	CH_4 (ppb)	CO (ppb)
CAL 1	386.34	1794.64	76.25
CAL 2	409.15	1947.13	153.70
CAL 3	448.38	2088.61	286.66
Target Gas	403.67	1962.70	135.97

Table 2: *Calibration and target cylinders used onboard SOOP COLIBRI.*

The regular measurement of a target gas of known concentrations is an essential component of the quality assessment, which is required for all ICOS stations. For the SOOPS COLIBRI and TAVASTLAND a target gas was measured 2 to 3 times per day (Table 3). Under flawless operation, both systems display a very similar performance, in line with the ICOS expectations.

For SOOP COLIBRI, we can distinguish between three periods (Table 3). The first period, right after the installation, was running as expected. After maintenance in the room hosting the analyser the biases and repeatability were degraded (Period 2 in Table 3). Finally the problem could be associated with a leakage in the pressure regulator used to deliver the target gas to the analyser. This problem may be due to the vibrations of the ship, or to the ship maintenance. However, the ambient air measurements were not affected by this issue. The target gas was changed in July 2020, but since there was no time to get the tank refilled and certified by the ICOS/CAL we had to provide a target gas filled and calibrated at LSCE central laboratory (Period 3 in Table 3). This has no impact on the measurement repeatability which is as good as before the leakage, but there is a larger bias to the assigned value, which is probably caused by the calibration being not perfectly consistent with the ICOS/CAL calibration scale. This result emphasizes the importance of using both calibration and target gases from the ICOS central laboratory to ensure the optimal compatibility of the measurement and their uncertainty estimates. It also confirms the stability of the analyser performances, which does not depend on the location of the ship (harbour vs sea; high latitude vs tropics).

TAV	**26-10-2020**	**20-11-2020**			
Species	**Mean**	**SD**	**Ndays**	**N injection**	**Inj. / day**
CO_2	-0.05	0.01	25	72	2.9
CH_4	-0.8	0.2	25	72	2.9
CO	3.9	1.5	25	72	2.9
COL	**28-01-2019**	**17-09-2019**		*Period 1*	
Species	**Mean**	**SD**	**Ndays**	**N injection**	
CO_2	0.00	0.03	173	498	2.9
CH_4	-0.2	0.1	173	498	2.9
CO	1.6	0.7	173	498	2.9
COL	**13-11-2019**	**22-07-2020**		*Period 2*	
Species	**Mean**	**SD**	**Ndays**	**N injection**	
CO_2	0.17	0.06	211	451	2.1
CH_4	-0.8	0.2	252	692	2.7
CO	3.9	1.5	252	692	2.7
COL	**22-07-2020**	**06-09-2020**		*Period 3*	
Species	**Mean**	**SD**	**Ndays**	**N injection**	
CO_2	-0.09	0.02	46	129	2.8
CH_4	-0.3	0.1	46	129	2.8
CO	3.1	0.5	46	129	2.8

Table 3: *Results of the regular injections of a target gas in the instruments installed on board TAVASTLAND (TAV) and COLIBRI (COL). The 'Mean' column represents the mean difference (in ppm for CO_2, and ppb for $CH_4$and CO) of the measurements with the assigned values by the central laboratory. For the COL we have splitted the time series into three periods. During the period 2, there was a leakage in the pressure regulator of the target gas. During the period 3 we have been using a target gas whose concentrations have been assigned by LSCE and not the ICOS/CAL.*

2.2.2 Systems using OTC-conform hardware for *p*CO_2 measurements

Historically seagoing underway systems for the determination of seawater *p*CO_2 are often measuring atmospheric CO_2 in regular intervals (typically for 5 minutes every 3 hours). This was often used to have an external check of the analytical system or to constrain local CO_2 fluxes between the ocean and the atmosphere. Normally, underway *p*CO_2 instruments are mounted in the ship's engine room to be as close as possible to the seawater intake. For getting atmospheric air to the instruments often long tubing needs to be drawn from outside to the engine room.

Depending on the ship, this tubing can be up to 100 m long, which is not different from a lot of atmospheric towers. This approach has not the same data resolution as a dedicated instrument for atmospheric measurements, but it opens the possibility to get data from areas where no atmospheric towers can be installed (e.g. open ocean). Furthermore, the atmospheric variability over the open ocean is lower than on land and interpolation can be done over bigger geographical regions. Most commercial vessels cruise with a speed of about 20 knots (37 km/h) or less which then translates to a spatial distance of approximately 100 km between two periods of atmospheric measurements.

2.2.2.1 Description of a classical OTC-conform *p*CO_2 system and amendments for high quality air measurements

A good description of the often used *p*CO_2 instrument from General Oceanics (Miami, USA) can be found in Pierrot et al. (2009), but most equilibrator-based systems have the same measurement principle: Water flows from the intake to the instrument, enters an equilibrator (spray head, bubble, laminar flow, marbles, …) and is discarded. Inside the equilibrator the air equilibrates with the seawater and is circulated through the instrument as follows:

> equilibrator → gas cooler (remove main water vapor) → pump (pumps the measurement air around, typically around 100 mL/min) → filter disc → Nafion dryer (remove water vapor) → multi-position valve → CO_2 sensor → equilibrator.

With the multi-position valve one can choose which gas is being measured (seawater equilibrated gas, calibration gas or atmospheric air). When an atmospheric air line is connected, the flow scheme is as follows:

> (1) air inlet → (2) atmospheric air pump (pumps constantly the atmospheric air to an air reservoir, flow rate ca. 400 mL/min) → (3) gas cooler (remove main water vapor) → (4) filter disc → (5) Nafion dryer (remove remaining water vapor) → (6) multi-position valve → (7) CO_2 sensor → (8) vent

As mentioned above the setup doesn't differ much from an atmospheric tower station. The data quality depends of course on the individual components, which are explained in detail:

1. Air inlet: in areas where the air temperature can fall under 0°C it is advisable to heat the inlet and the part of the tubing that is outside the ship's structure. It was shown that using a downward pointing open container (like a cut water bottle) filled with filter wool improves the precision of the measurements. This might be due to the fact that the filter wool keeps salt particles out of the tubing.
2. Air pump: any air pump can be used that produces high enough air flow.
3. Gas cooler: Simple Peltier cooler to dry most of the water vapor out of the gas.
4. Filter disc: Regular filter disc (0.2 µm) to prevent humidity or particles from passing.
5. Nafion dryer: When using an NDIR instrument the measured gas is supposed to be dry as it is not an easy task to continuously calibrate the water channel (or NDIR cells without water channel are used). When using laser based instruments that can measure the water vapor and correct the CO_2 measurement reliably, the Nafion dryer can be omitted.
6. Multi position valve: explained above.
7. CO_2 sensor: The use of laser based CO_2 detectors in this kind of underway installations is to date not fully implemented. But it is clear that the use of a more accurate CO_2 sensor improves the resulting CO_2 measurements.

An assessment of the system installed on the SOOP ATLANTIC SAIL is given in Section 3.3.3.

2.2.2.2 Choice of calibration gas set up

For oceanic pCO_2 measurements the minimum amount of non-zero calibration gases is two, while the recommendation is three. The gases have to bracket the expected concentration range which results often in a minimum calibration gas with 200 ppm CO_2 and a maximum gas with 500 ppm CO_2 (open ocean conditions). The third gas is often chosen to be somewhere in the middle between the highest and the lowest calibration gas. When aiming for high quality atmospheric CO_2 measurements the middle calibration gas should be chosen close to the atmospheric value or a fourth gas should be added. In addition, according to ATC standards, a target gas needs to be included (see Table 4).

	for zeroing IR sensor	lowest STD	middle STD	target	high STD
Only oceanic measurements	0	240 (±20)	380 (±20)	-	530 (±20)
Oceanic and atmospheric measurements	0	240 (±20)	410 (±5)	410 (±5)	530 (±20)

Table 4: *Example for a set of calibration gases when using the instrument in the classical (oceanic) mode or with additional measurements for the atmosphere. All values are in ppm.*

The additional calibration gas measurements mean that the calibration routine takes longer and less environmental data will be measured. When using an NDIR instrument the recommendation is to measure a set of calibration gases every three hours. When using a laser-based detector this interval might be extended as shown for atmospheric applications, so that the longer calibration periods wouldn't affect the environmental data too much. These kinds of sensors are not well established in the ocean community yet. As more and more oceanic stations are using laser based instruments from different manufacturers, we are optimistic that the international standardised measurement protocols (e.g. SOCAT) will be adjusted and less frequent calibrations will be required.

Figure 1 shows a typical measurement sequence when using a seawater pCO_2 system. The aim is to change between different gases as seldomly as possible, because for every change of gas the sensor and gas lines need to be carefully flushed and no data are recorded.

gas	remark	measurements in min
zero	Zero gas, only needed for NDIR instruments	1
span	Highest calibration gas, only needed for NDIR instruments	1
low STD	Lowest calibration gas	3
mid STD	Middle calibration gas	3
high STD	Highest calibration gas	3
target STD	Target gas from CAL	3
ATM	Atmospheric air	10
EQU	Air equilibrated with seawater	150
low STD	Lowest calibration gas	3
mid STD	Middle calibration gas	3
high STD	Highest calibration gas	3

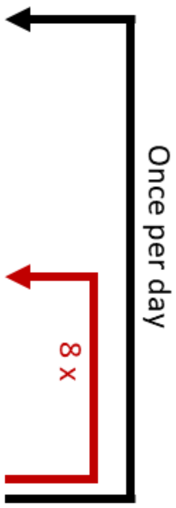

Figure 1: *A typical measuring sequence using a seawater pCO_2 measurement system. The first two lines can be omitted when using a laser based CO_2 detector. But the principle is always the same. A run of calibration gases is followed by the target gas and 10 minutes of atmospheric measurements. Then it is followed by ca. 3 hours of seawater measurements before it starts again with a calibration run.*

2.2.3 Ship (and transit line) specific considerations

Apart from the gas analytical system and the specification of calibration gases and their running sequence for the two applications addressed in Sections 2.2.1 and 2.2.2, several recommendations specific for the installation on SOOP lines in general can be given.

<u>GPS, Time, Data Transfer, and Remote Access</u>

The exact time and position of a measurement is obviously a mandatory requirement for measurements on a moving platform. The use of a time server is recommended for time synchronization of the analyser and all system components. Time server / GPS systems are available in one device for rack mounting. Depending on the ship's route, the system might be offline for longer time periods, and connection to the ship's IT infrastructure (LAN) is often prohibited. Thus, a minimum of automatization is recommended, including provision of data transfer at least during port calls, as well as remote access to control valves and switches, to assure a safe shut down or even restart of the system, or change routines such as e.g. the measurement protocol of calibration and target gases remotely. With the carrier often out of reach for weeks to months, provision of external control can substantially increase the duration of successful data collection.

<u>Set-Up location and connection to the ship</u>

The identification of the location for any installation is crucial. Space is a rare commodity on a commercial vessel, and regulations concerning escape routes are stricter than on land. Compact design in a way allowing easy demobilization is recommended (the ship might be decommissioned or change its routine journey), and robust connection to the ship (usually by welding) must be assured. It should be possible to anchor the system at the place of installation to protect the crew and the system itself. Suitable surfaces, eye holes or welding points must therefore be available or, if necessary, created first. The installation including the gas bottle rack has to be secured even under ship-endangering sea conditions.

It also has to be clarified how e.g. the power supply on the ship is specified, whether enough (safe) power sockets or a WLAN or LAN connection exists. Basically all commercial ships encounter occasional power failure and short blackouts, so a UPS unit for the entire setup is strongly recommended, not to say mandatory. Rooms even inside a vessel can encounter strong temperature and humidity fluctuations, so the designated installation room should be evaluated in that regard to avoid overheating, condensation or other surrounding parameters for which main components of the installation are not classified. All ventilation must be protected, as cleaning, rust removal etc. on a ship can frequently lead to fine particle contamination. The influence of ship vibrations on the overall system can be severe and lead to decreased lifetime of components, higher leakage rate, or compromised data quality. So far, however, the installations described in this report did not show any restrictions due to ship vibration. Also the influence of the measuring system itself on its environment (waste heat, vibrations, noise, weight of the system etc.) should be considered; in particular if the room if frequently used by the ship's crew. A central main emergency switch is also recommended.

<u>Air inlet location and design</u>

As already indicated above, in most cases it will be impossible to locate the sample air inlet as well as the meteorological station at a height of 10 m above sea level. The location of the air inlet is a compromise between distance from the ship's exhaust and requirement to stay out of the area of severe sea spray in heavy winds. Weather shields to protect the air inlet normally work only for water that comes from above. Thus, the air intake should as well not be placed too exposed, e.g. outboard, as this can either lead to water ingress or, in the worst case, to damage of the air inlet and tubing in heavy winds and stormy seas. This is even more the case if the inlet and pipes are insulated and heated. In colder climates (e.g. northern parts of the Baltic Sea), heating of the inlet and piping slightly above ambient temperatures might be necessary to avoid condensation of water inside the air tubing and to prevent the inlet and adjacent filters from freezing.

In contrast to land-based measuring systems, at sea it is possible that not only rainwater but also saltwater can enter the air pipes via the air intake (e.g. sea-spray). Mechanical parts in the air flow path, such as solenoid valves or multi-position valves, are particularly at risk, as crystallized salt particles can deposit here and damage valve seals or rotors through increased abrasion or blockage. Therefore, inlet filtering and the provision of water protection switches and protective valves can be advantageous for such systems at sea. In all cases, the design of the air inlet path should be approved by the ATC.

2.2.4 Integration into the ATC data processing stream

The data produced by the analysers, the GPS system and the meteorological sensors are transferred to the ATC server when the vessels stay in a harbour. Data from the analysers and the meteorological sensors are processed using the ICOS data processing programs independently from the fact they were produced on a moving platform.

The program processing the analyser's data uses the unsynchronized files produced by the (Picarro) analyzer. The transfer bandwidth can be reduced by only selecting the required subset of the columns from the default forty columns. The program processing the meteorological data uses an ATC-defined ascii format. The wind, pressure and relative humidity data averaged at one Hertz are to be provided in a single file. The speed of the vessels allows computing meaningful hourly means.

The processing and the tracing of the data need metadata to be entered in the ATC database beforehand. As an example, all instruments providing data to be processed by the ICOS ATC system need to be registered and assigned a unique identifier; this identifier is used in the naming of the data files.

The data produced by GPS systems provide the information on the ship movement. The format used is a simple text file with the date, time, latitude, longitude and altitude (AMSL). In order to be processed by the ATC system, the data come along with a simple journey metadata file listing the operators, the beginning and end of the journey identified by a unique identifier. A journey can be defined as transect like for the SOOP TAVASTLAND or something larger like for the SOOP COLIBRI. A post-processing algorithm will be implemented to automatically define areas like ports, coast or ocean transects (see chapter 2.2.6 for more information).

Metadata entered in the ATC database allow for making the link between the GHG data or meteorological data and the position of the vessels given by the GPS systems. Examples of the data records of the SOOPs COLIBRI and TAVASTLAND are given in Figures 2ab.

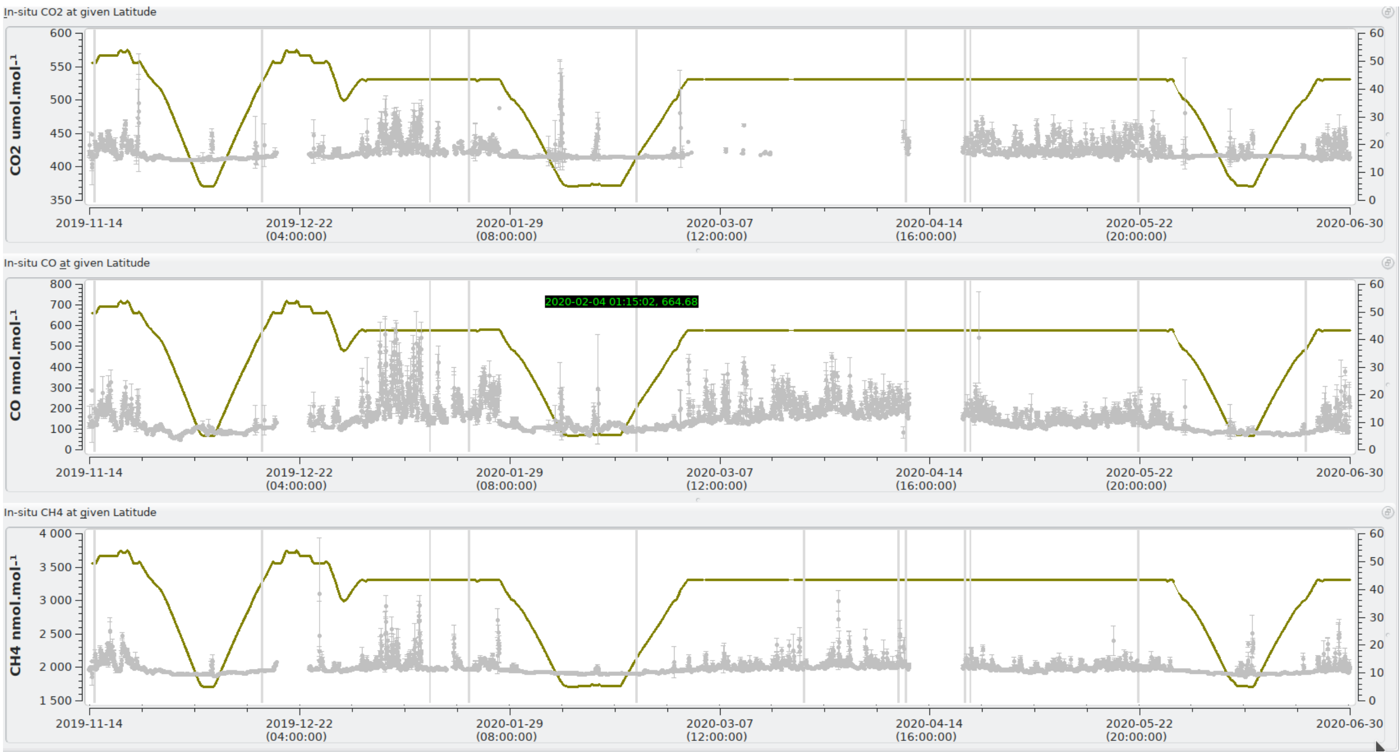

Figure 2a: *Data recorded by SOOP COLIBRI after ATC processing from Nov. 14th 2019 to June 30th 2020 as hourly means. The latitude of the position of the measurement is overlain (green line and right hand axis), indicating the position of the ship.*

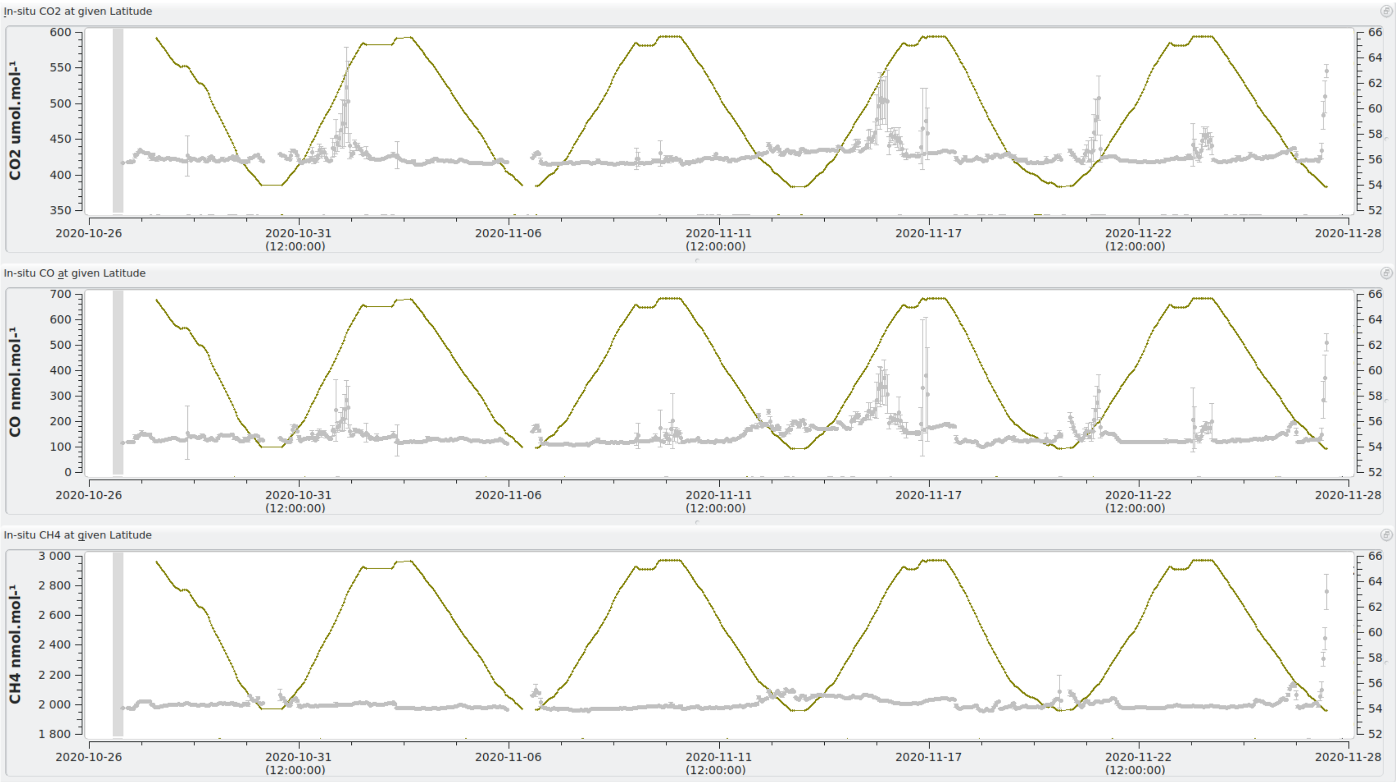

***Figure 2b:** First five weeks of data recorded by SOOP TAVASTLAND after ATC processing from Oct. 27th to Nov. 28th 2020 as hourly means. The latitude of the position of the measurement is overlain (green line and right hand axis), indicating the position of the ship.*

2.2.5 Data post-processing

As the instrument measures the ambient air constantly, we end up with a dataset combining atmospheric observations made both in the ports and in the middle of the sea, with very different variabilities. In order to facilitate the data analysis, we have evaluated an algorithm to select atmospheric measurements, depending on whether the ship is in or near a port; along the European coasts; or in an Atlantic transect for SOOP COLIBRI (Figure 3a). For this data selection we have entered in the database the coordinates of the harbours where the COLIBRI makes stop, and we separate the measurements along the European coasts, and the trans-Atlantic crossings by using coordinates also entered in the database. Harbour windows have also been assigned for SOOP TAVASTLAND.

In addition to this selection of data according to the position of the ship, we have also validated the use of CO measurements as a tracer of local contamination from the ship's exhaust. For this step we use the spike detection algorithm set up in the ICOS data processing (El Yazidi et al., 2018). With this statistical tool applied to the COLIBRI dataset (first year), we detect spikes in about 30% of the hours when the ship is located in a port, 9% when it is close to the European coasts, and 6% during the trans-Atlantic crossings (Figure 3b). A preliminary accounting of the spikes for the SOOP TAVASTLAND in the Baltic Sea indicates that about 6% of the minute averaged data are detected as a spike for the Baltic Sea observations from 31 Oct. to 20 Nov. 2020. For a longer observation period on board the COLIBRI (March-Sept.2020) this same statistics amounts to 4%. Even if a more detailed analysis of the TAVASTLAND dataset needs to be performed with a longer time series, those close values indicate that the percentage of data significantly contaminated by the ship’s stack remains pretty low in both cases.

Those developments have been tested and will be implemented in the ICOS/ATC database in the coming months, for a systematic data selection process. In the longer term, it would be interesting to associate a calculation of back-trajectories with the positions of the ship in order to help the interpretation of the observed variabilities. An example of these calculations, based on the use of the Hysplit model (Stein et al., 2015) applied to the COLIBRI transect in August-September 2019, is given in Figure 4, showing that a large part of the fast variabilities observed during the transects are related to the origin of the air masses.

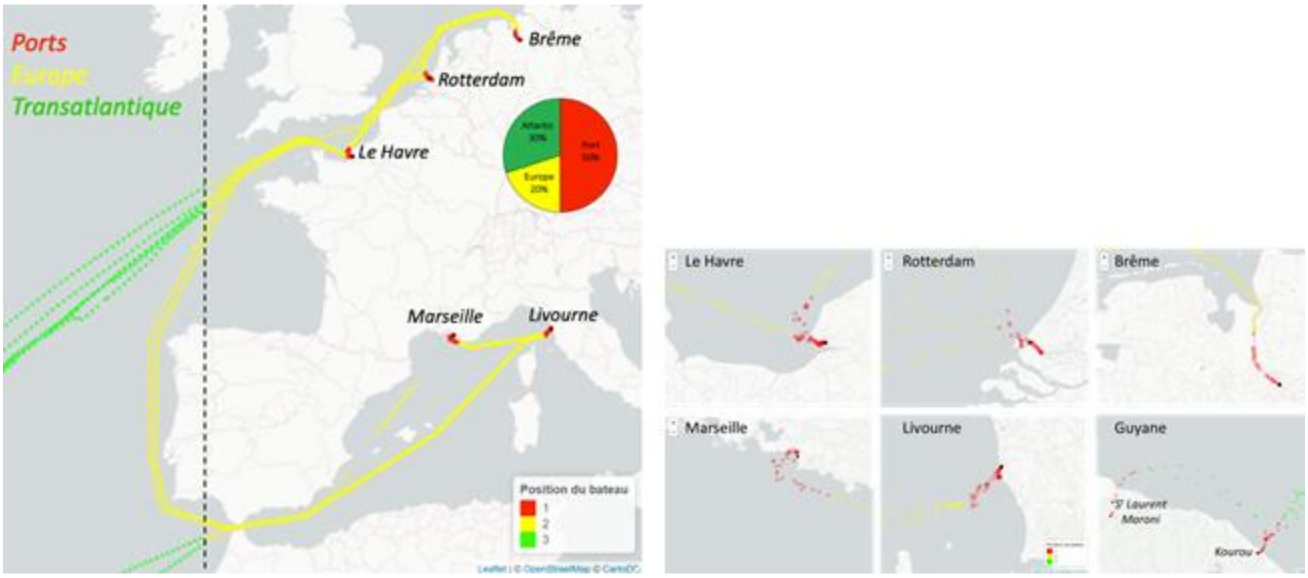

Figure 3a: *Left: Data selection in three categories depending on the vessel location. Right: zoom on the main harbours including ship locations within ±30km (red dots).*

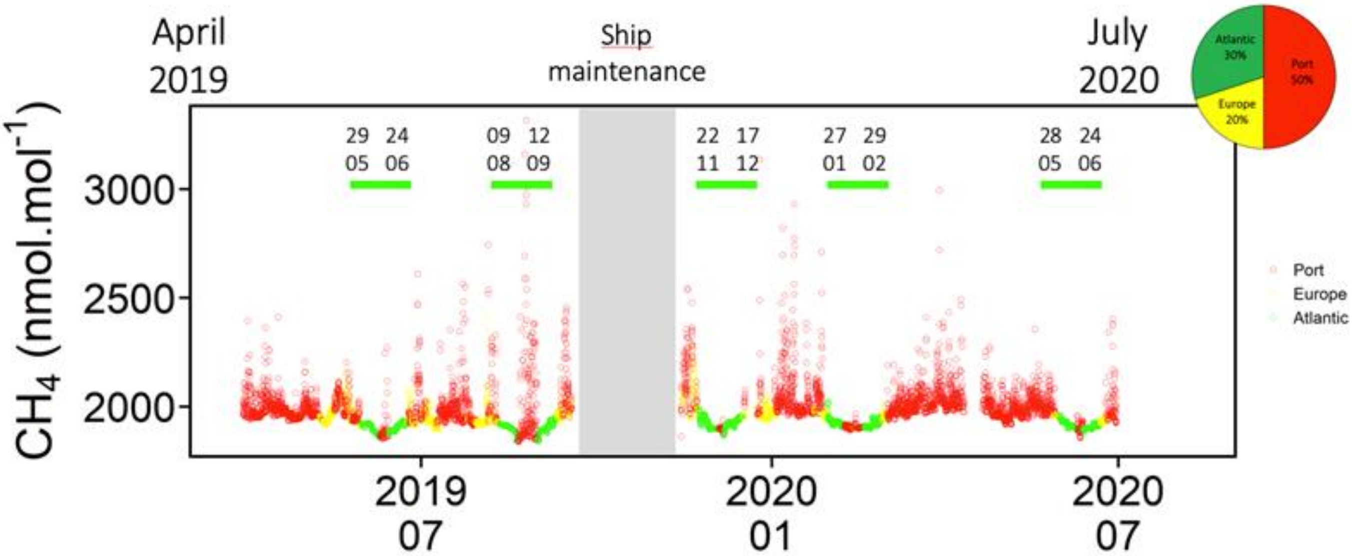

Figure 3b: *CH_4 time series from the first year of COLIBRI observations, with the colours indicating the position of the ship. The green bars represent the back and forth transects between France and Guyana.*

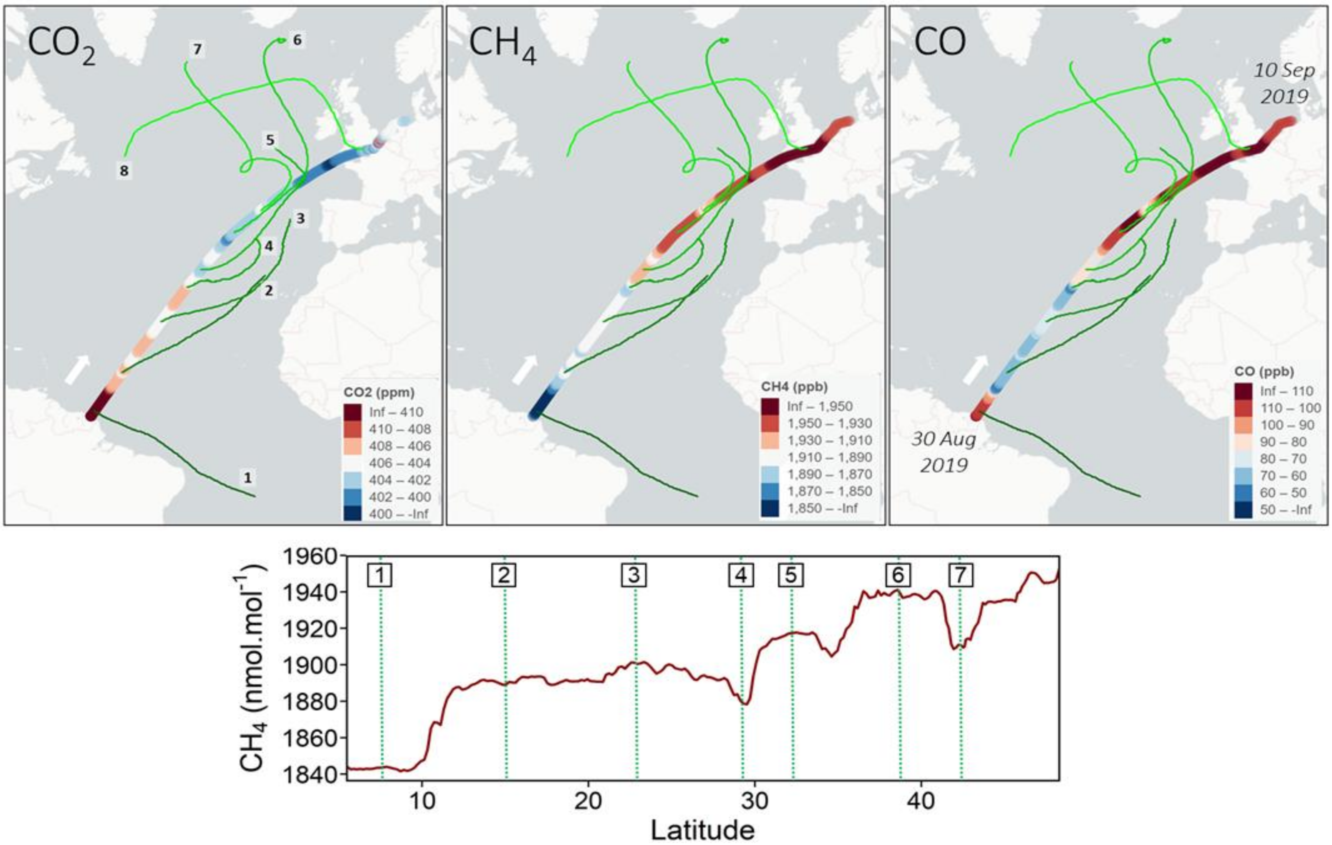

Figure 4: *COLIBRI transect from French Guiana (30 Aug.2019) to Europe (10 Sept.2019). Above panels show the CO_2, CH_4 and CO concentration maps, with eight back-trajectories. Below figure shows the CH_4 concentrations, with the timing of the back trajectories.*

3 ASSESSMENT OF IMPLEMENTATION OF ATC-CONFORM PLATFORMS

3.1 Introduction

In the following, the technical realization of the three installations for atmospheric greenhouse gas concentrations on SOOP lines are documented, and, as far as already possible, evaluated. Due to some obstacles, including access and operation of the vessels, delay in instrument delivery and finally, restrictions for finalization and maintenance due to the Covid 19 pandemic, all systems were operational after an unforeseeable delay with respect to the original work plan. Still, at this point, all systems are operational and at least the performance of the installation on SOOP COLIBRI can be fully evaluated. The installation on SOOP TAVASTLAND was operational approximately 5 weeks before finalizing this report, and the results are shown in Section 3.3.2 and already proof the operation matching ICOS ATC standards. All lines will remain operational in the near future and the measurements will be maintained once the RINGO project has ended. This will allow a full evaluation of the long-term operation and scientific added value.

3.2 Overview of implemented infrastructure

The major routes of the three lines are indicated in Figure 5. The overview map underpins the very different nature of the lines in terms of climatic conditions, length of transit, and part of the journey spent at open sea, coasts, and harbours.

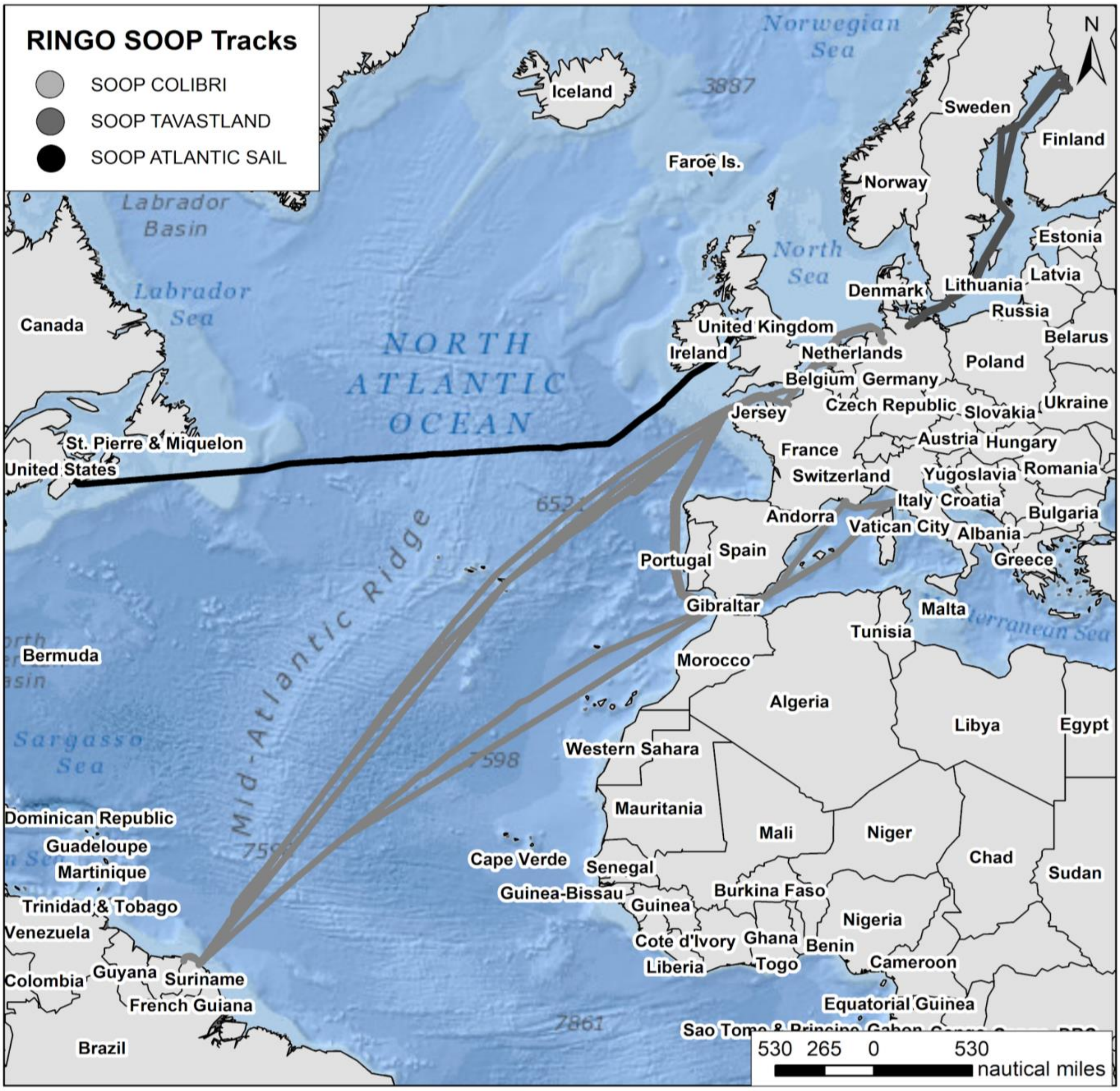

Figure 5: *Map of the three SOOP Lines, the vessels COLIBRI (IMO: 9207390), a RO/RO cargo ferry designed for the purpose to transport parts of the European Ariane rocket , TAVASTLAND (IMO: 9334959), a RO/RO cargo ferry (Hazard A - Major) and ATLANTIC SAIL (IMO: 9670585)), a RO/RO container carrier.*

3.3 Individual platforms

3.3.1 Installation on SOOP TAVASTLAND

The SOOP TAVASTLAND (IMO: 9334959), a RO/RO Cargo Ferry (Hazard A - Major, see Fig. 6a**)**, crosses nearly all major basins of the Baltic Sea twice in seven days. The route (Fig. 6b) includes the ports of Travemünde (Germany), Oulu (Finland), Kemi/Ajos (Finland) and, depending on the ship's timetable, occasionally the port of Husum (Sweden).

Figure 6: *left - SOOP TAVASTLAND (IMO: 9334959), a RO/RO Cargo Ferry (Hazard A - Major), the arrow marks the location of the air inlet; right - cruise track (round trip) of the vessel usually completed in exactly one week.*

<u>Installation overview</u>

The system for ATC-conform atmospheric measurements on SOOP TAVASTLAND is built entirely into a 19” steel rack. SOOP TAVASTLAND provides power supply. Unfortunately, the ship's internet connection (WLAN) is unreliable and too slow, and therefore not an option for remote access to the system. Thus, a stand-alone solution for the remote access to the system is tested since Oct. 27th 2020 (mobile network connectivity with prepaid SIM-Card) to allow remote access system checks, necessary adjustments and data downloads at port calls of the ship in Travemünde (Germany) and Oulu (Finland) or Ajos (Finland).

A description of the technical realization used on SOOP TAVASTLAND is shown in Figure 7, including a list of the main components. More information on the components and parts used for the setup are provided in Appendix A1. The required standard gas cylinders (up to 5 Luxfer, 20 L aluminium bottles) are set up together with the measurement system in the crew fire-fighting preparation room. The gas cylinders and regarding pressure reducers required for the system are mounted in a stand-alone gas cylinder rack, specially manufactured for this purpose by the IOW workshop.

During a three weeks test run in the laboratory at IOW, the whole system was tested under different ambient conditions. As one result, the system is now equipped with additional fans and ventilation openings for heat dissipation, and safety shutdowns are installed to prevent hazards in the event of excessive heat inside the cabinet. Some additional options for remote control of some vital switching states are also installed, such as e.g. the emergency switching state of the water-guard-triggered solenoid valves, the switching of the uninterruptible power supply (UPS) and its states / shutdown, the proper shutdown of the Picarro analyser, the switching of the air-pump circuit and the regulation of all flow-controllers. The control of the regarding software is adapted accordingly.

In collaboration with chief engineers of SOOP TAVASTLAND, the setup of the system cabinet and gas bottle rack in the room was optimized for best access of all vital parts, including the UPS, the Picarro analyzer, the GPS and time-server, the data acquisition unit and all pumps and other sensors and switch boxes in the periphery. This had to be realized assuring also minimal spatial restrictions for the crew, as the room has to be used by several people at the same time in case of a fire-fighting exercise. The construction of the entire set up would allow for a quick swap of vessels at a later stage.

The system hosts two air lines of ~30 m each to allow for quick troubleshooting and as well as for comparison / reference measurements with ATC's mobile reference system. All tubings outside the system, in particular those that are attached to the ship's superstructure, are isolated and heated in order to avoid water condensation and ice formation. The air tubing was installed with as few bends as possible (no sharp bends or kinks!) and with a constant gradient towards the measurement system, in order to avoid areas of condensed water collection inside the tubing, which would enhance the risk of water entering the measurement system and delay of the CO_2 signal. The intake was placed in the immediate vicinity of the weather station's sensor holding frame. The location of the air inlet is a compromise between distance from the ship's exhaust and requirement to stay out of the area of severe sea spray in heavy winds, which on the Baltic Sea), even on high ships as the TAVASTLAND, can be blown easily vertically from the waterline of the ship up over the highest platform, depending on wind force and direction. Weather shields to protect the inlet were designed and manufactured as in kind by the ATC. Assessment of a longer period of measurements (currently five weeks) will show whether a relocation of the air inlet would be needed, though the options on the ship are very limited.

Systems to be installed on ships have to be designed not only with maximum safety for the built-in hardware (e.g. the Picarro G 2401) but also for the crew of the ship, and the electrical and data circuits of the vessel. Final functional and safety tests were performed on the spot after installation on the SOOP TAVASTLAND, and all built-in safety and emergency cut-off facilities are checked frequently during long-term operation of the system.

Weather data are measured and recorded, using an automatic weather station from SMHI, already installed on the ship, with the corresponding required sensors (humidity, temperature, wind speed and -direction), installed on the outer deck above the ship's bridge, near the air inlet. Unfortunately sensors for wind velocity and direction are currently not installed, and the current sensors do not all have conformity with ATC specifications, as the weather station was equipped several years before the realization of the trace gas analytical system described here. On the same location, an autonomous GPS antenna for the position and time server is installed.

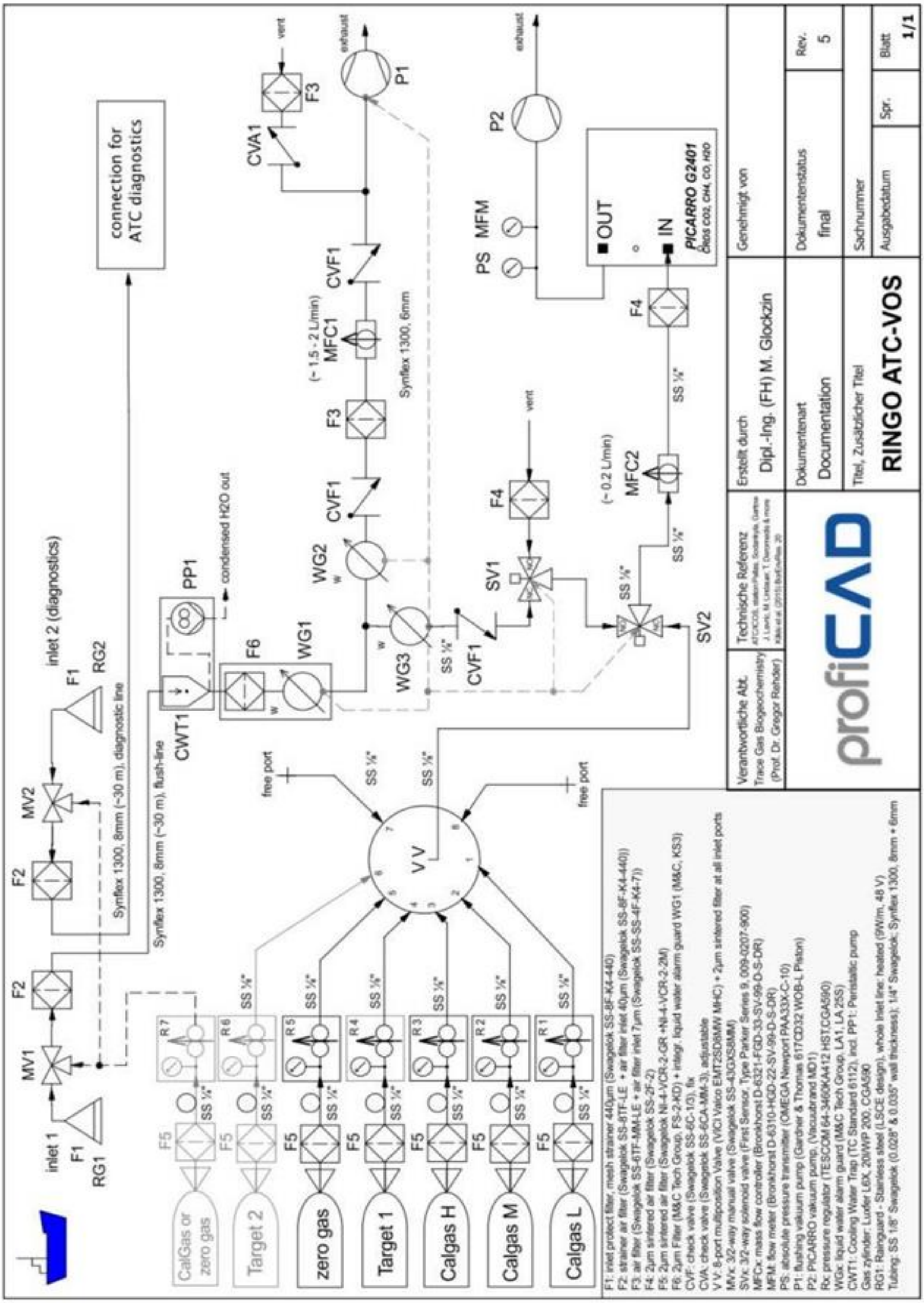

Figure 7: Schematic drawing of IOW RINGO-ATC-SOOP system on SOOP TAVASTLAND, with list of actual parts.

Installation details:

Ambient air is continuously drawn in through a ~30m-long tubing (Synflex 1300, 8mm) that is isolated (Armaflex), heated (~5-15W/m, DC power supply <=48 V 10 A max. for safety reasons) and dried down to an H_2O content of < 0.9% (Buehler Peltier cooler). An aliquot of it is branched off to the gas distribution system (Swagelok 1/8" stainless steel line), and then led into the Picarro G2401 sensor for determination of CO_2, CH_4, and CO mole fractions. Both the continuous ambient air flow as well as the measuring gas flow are regulated and monitored using mass flow controllers (Bronkhorst). Behind the Picarro analyzer and in front of the Picarro vacuum pump, a pressure transmitter (Omega) monitors the pressure in this line. Between the analyser and its vacuum pump, a mass flow meter (Bronkhorst) monitors the exhaust flow. The time for the air travelling from the inlet into the analyser cavity is almost exactly one minute. In this circuit, a nafion dryer can be introduced to further lower the level of moisture, but this adds to the dead volume and leakage possibility. Furthermore, one must be very careful how and where to introduce the dryer, as switching of valves under low pressures and resulting backpressure / pressure peaks can easily destroy the membranes inside a counterflow-nafion-dryer.

Air filters and check valves (Swagelok) are implemented at neuralgic points to protect pumps, magnetic valves and sensors against damage from minute particles, too high differential pressures, and backlashes. Water guard sensors protect the regarding hardware from water damage by switching magnetic valves and motors accordingly. The special requirements on SOOP lines concerning the protection of the air inlet against contamination by water and salt is emphasized in Chapter 2.2.3. Calibration gases and target gas are distributed via a VICI multiport valve (dead-end), controlled by the Picarro analyser software. Data is recorded internally within the Picarro sensor. Moreover, the data flows from this and all other sensory units are recorded by a portable computer and an appropriate software solution.

During test runs and since the onset of regular operation on TAVASTLAND on Oct. 27th 2020, the data structure and any necessary adjustments to comply with the ATC formats have been clarified and taken into account to ensure data delivery to the ATC. To minimize unnecessary ship control visits, and to have at least a minimum amount of control over system status by remote access, a National Instruments USB-6221 multi I/O unit is built in to function as interface between e.g. switching relays to control parts of hard- and according control software or to monitor safety relays (e.g. water guards). This allows not only for simple system monitoring but as well opens the possibility for a rudimentary remote system control of e.g. the switching of lines that are vital for a safe shutdown of the Picarro analyser, VICI valve control, flow controller adjustments as well as UPS monitoring and shut down. The analyser can be shut down safely and the whole system then be shut-off remotely. Finally, hard-wired automatic emergency shut-offs secure either partial or entire system shut-down, depending on the severity of the fault.

Calibration gas supply:

The calibration gases have been delivered by the CAL according to ATC protocols (see Table 5). All gas regulating and carrying components strictly follow ATC requirements (for components see Figure 7). Due to the test site character of the instrumentation, no long-term target has been integrated, but the peripherals for the long-term target is already foreseen in the construction (see Figure 7).

Cylinder ID	CO_2 (µmol/mol)	CH_4 (ppb)	CO (ppb)	MPV Postion (Port)	time calibration (minutes) repeated 4 times/ 30 days	time air meas. (minutes)
CAL 1	420.30	1970.81	158.13	1	-	20
CAL 2	380.82	1797.17	75.00	2	30	-
CAL 3	405.75	1949.11	150.76	3	30	-
Target Gas	448.97	2079.55	244.66	4	30	-
ATM				6	-	460

Table5: *Concentrations and identifiers of the set of four calibration gas bottles provided by ICOS CAL in operation on SOOP TAVASTLAND, with sample times and intervals.*

Current Status:

The whole electrical interface, wiring and programming were completed , tested and approved, and a long-term test was carried out at IOW under natural conditions for three weeks in June 2020. All main components have been onboard since September 2020, and the rack and cabinet were welded onto the floor by the crew for maximum security. Reassembly of the tubing and electrical connections were done at times when the ship was at the harbour in Lübeck (approx. six hours on Fridays), and a one-week long roundtrip, both with only one technician, due to COVID-19 restrictions.

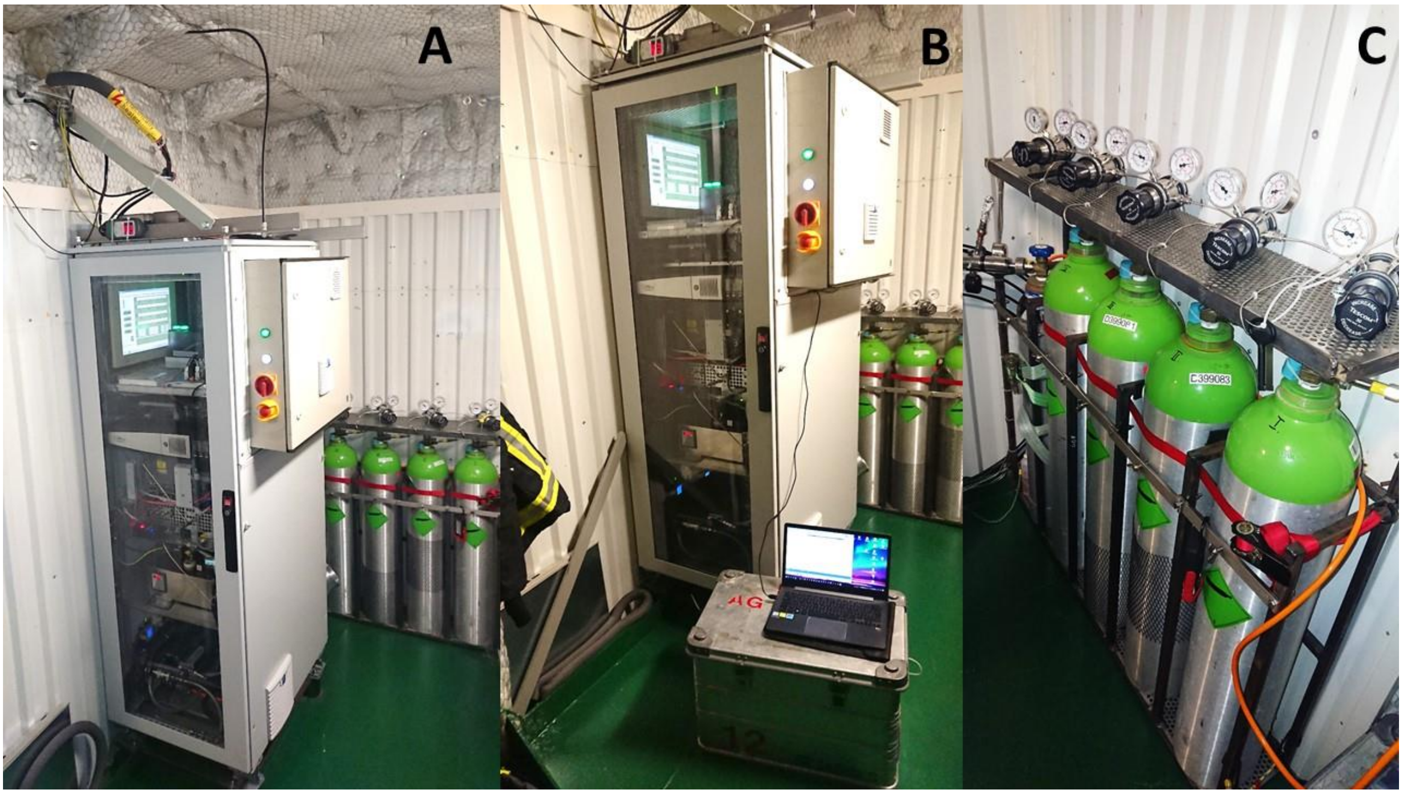

Figure 8: *Final placement on board SOOP TAVASTLAND -* ***A****: entire system, running and 19" cabinet closed;* ***B****: system controlled with external laptop via ATEN KVM USB Switch* ***C****: gas bottle rack with pressure regulators.*

The insulated heated air tubing / air inlet and the electrical wiring were pre-built in the laboratory at IOW and then completed on board (Figure 9). With the system running, the heating of the tubing was assembled and tested, and is now running to avoid freezing and condensing of water inside the air inlet and the air tubing in case temperatures below freezing point are encountered (Figure 10). The heated air tubing is following a design which has been successfully employed on Finnish atmospheric stations (Tuomas Laurila, FMI, pers. communication and Kilkki et al. 2015).

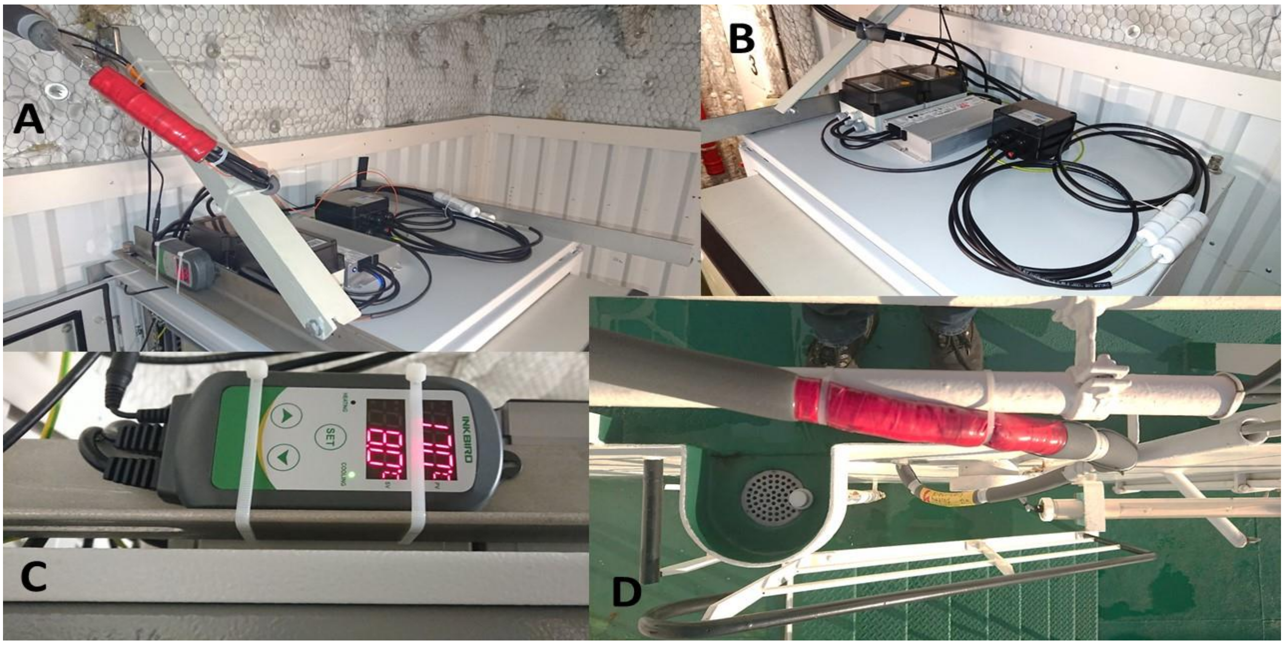

__Figure 9:__ Air line heating system - __A__: self-built heating system with power supply, fuse boxes and heating line installed on top of 19" cabinet; view from front; red tape marks the location of the temperature sensor for emergency shut-off of the heating (shut-off temperature freely selectable); __B__: heating system with power supply, fuse boxes and heating line installed on top of 19" cabinet; view from behind __C__: heating control unit regulator (shut off temperature freely selectable); __D__ : air line after ship wall lead-through, red tape marks the location of the temperature sensor for heating control unit for outside air tubing temperature.

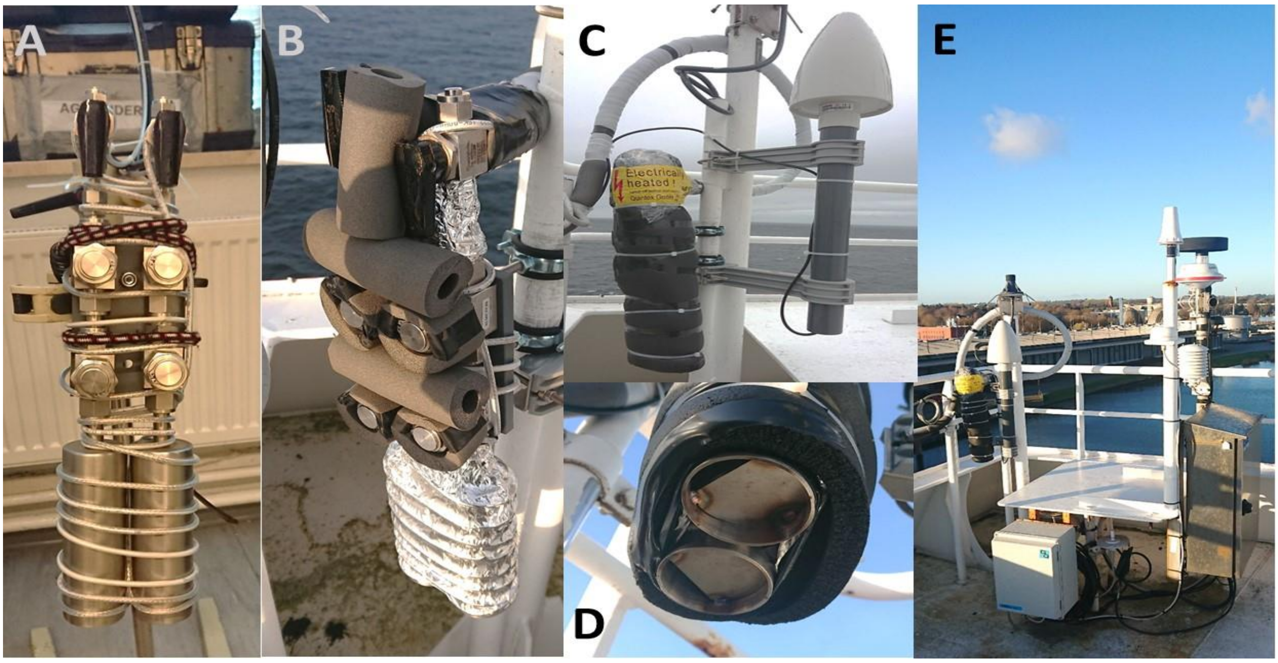

__Figure 10:__ Heated air line and air inlet on board SOOP TAVASTLAND - __A__: pre-building of the heated air line and -inlet in the IOW laboratory (shown here: inlet only), weather shields kindly provided by ATC; __B__: isolation with aluminium adhesive tape and armaflex tubing; __C__: heated and insulated air inlet (GPS antenna on right side); __D__: air inlets of weather shields, only one is active at a time, the other one serves as spare and diagnostic line; __E__: place of installation on board TAVASTLAND near SMHI weather station, the point on the (portside) top deck furthest from the ships exhaust.

First data evaluation and quality assessment

The target gas measurements (see Section 2.2.1.3)enable an evaluation of the analyser repeatability and the possible bias of the calibration function. It does not provide a full assessment of the measurement uncertainties since the water vapor correction and possible biases or leakages in the inlet line dedicated to the ambient air are not evaluated with the target gas measurements. We face the same issue at the ICOS surface sites, where a more complete assessment of uncertainties can however be done thanks to side-by-side measurements with regular flask sampling, or with the ICOS mobile lab on a campaign basis. In the case of the SOOPs we do not have duplicate measurements to be compared with. Still we can compare the consistency of the SOOP measurements with ICOS sites located in the same area. In Figure 11 we present the time series of the SOOP TAVASTLAND with two ICOS sites in the Baltic Sea area: Utö on a small island in Finland, and Svarberget in Sweden. Overall we observe similar synoptic variabilities for CO2, CH_4 and CO, but as expected the measurements from the ship show stronger spikes, corresponding to the periods in the harbours. If we restrict the comparison to the few hours (12 hr) when the ship is passing relatively close to Üto we can calculate a mean difference of +0.8±1.4 ppm, -1.0±2 ppb and -0.9±3.7ppb respectively for CO_2, CH_4 and CO (Figure 11, right panel). Those results indicate a good consistency between the two dataset for CH_4 and CO, but higher CO_2 concentrations on board the ship (not due to local contamination by the ship stack which would be seen also for CO). Clearly more observations will be needed for reliable statistics since the CO_2 differences show strong variability from one day to the other. This evaluation of SOOPs measurements with background ICOS sites needs to be implemented in the ATC database for a more systematic evaluation.

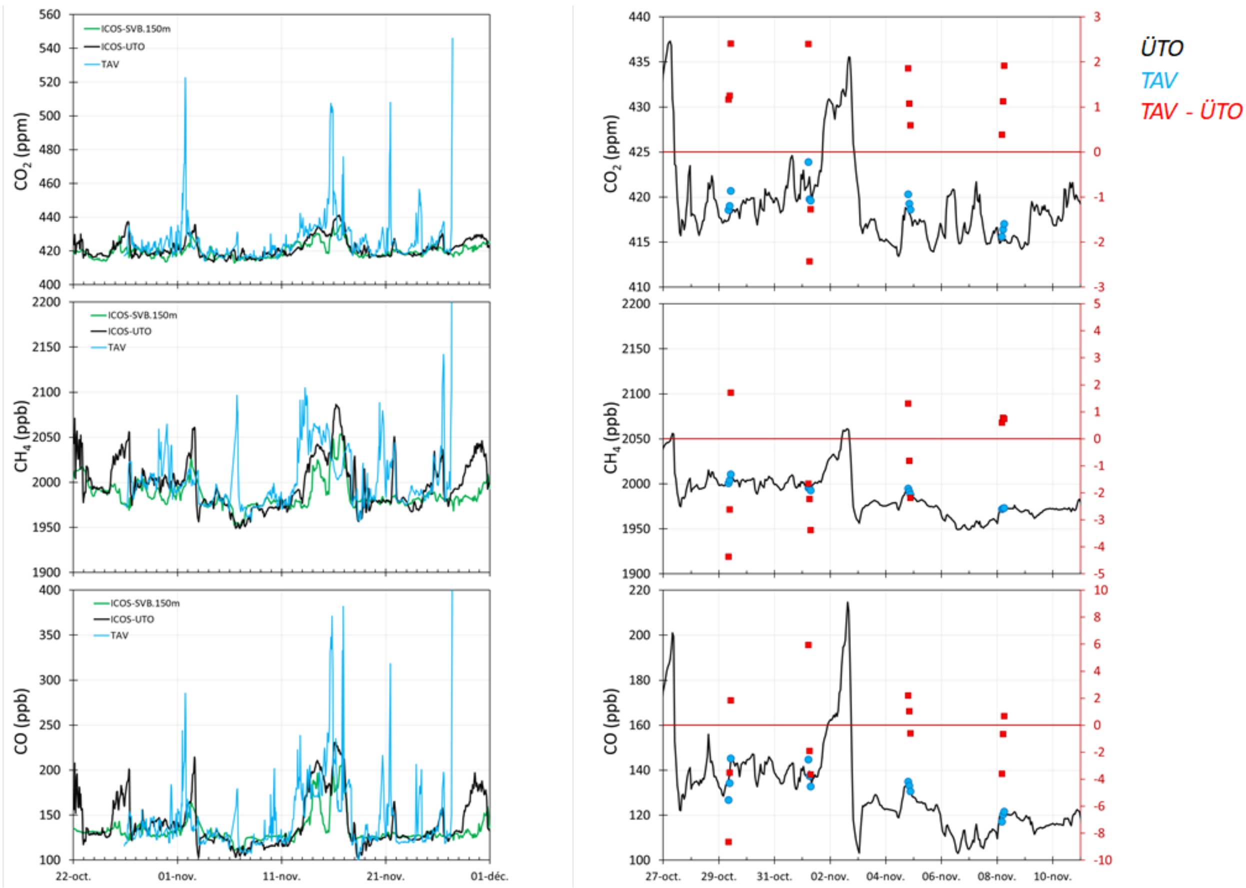

__Figure 11:__ Left panel: CO_2, CH_4 and CO concentrations monitored on board the SOOP TAVASTLAND (blue), and at the ICOS stations of Üto (black) and Svarberget (green) in the Baltic Sea. Right panel: comparison of the concentrations at Utö, and on board TAVASTLAND when the ship is passing close to Üto Island. Differences are shown in red.

3.3.2 Installation on SOOP COLIBRI

The SOOP COLIBRI is a large vessel (115 meters length, 20 meters width, Figure 12a) that is dedicated for the transfer of the European Ariane rocket parts between Europe and the launching base of Kourou in French Guiana (Figure 12b). Therefore, the ship that is primarily attached to the harbour of Marseille in the Mediterranean Sea also frequently moves to Le Havre in the North Sea (France), Livorno (Italy), Bremen (Germany) and St. Petersburg (Russia) to collect parts and/or equipment before crossing the Atlantic Ocean. The ship is equipped with a setup dedicated to measure the partial pressure of CO_2 in surface waters since several years (Lefèvre and Diverrès, 2017). It also hosts a full weather station run and processed by Météo-France and fulfilling all WMO (World Meteorological Organization) measurement standards.

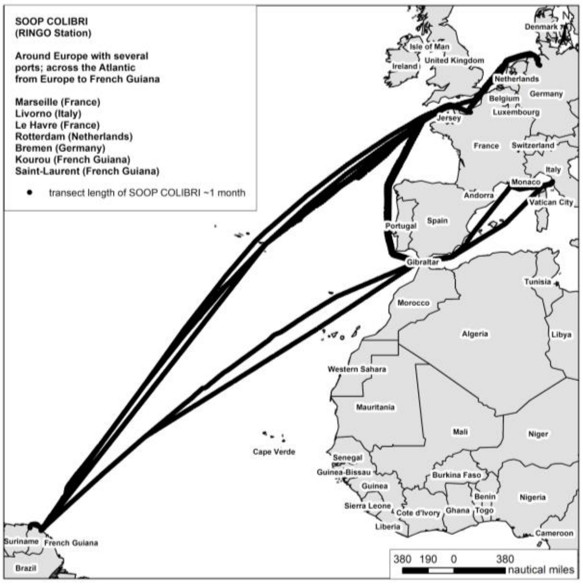

Figure 12: *left - SOOP COLIBRI (IMO: 9207390), a RO/RO Cargo Ferry; right - transects around Europe and across the Atlantic.*

The setup for ATC-conform measurements of atmospheric air on board SOOP Colibri consists of the following elements:

- air inlet and air tubing;
- greenhouse gases analyser (CO_2, CH_4, CO, H_2O cavity ring down spectroscopy analyser, Picarro G2401);
- set of calibration and quality control compressed air cylinders (4) provided by the CAL from the ICOS-RI connected to a multi-position valve enabling the sequential measurement of the different cylinders and atmospheric air;
- GPS to recover real time positioning of the vessel and absolute time stamp;
- back-up system to ensure the data safeguard;
- uninterruptible power supply to preserve the equipment in case of power fluctuations or shut-down;
- 4G router used for data transfer during the time the vessel stays in a harbour.

The measurement system has been integrated in a compact rack located on the lower third deck of the ship (Figure 13). The rack has been welded onto the deck, as well as the cylinders supports. The cylinders are retained by adjustable strips to the supports in order to prevent any movement in case of heavy sea conditions. All equipment inside the rack is fixed for the same reason and also to avoid too many vibrations during navigation. However no specific instrumentation, compared to an ICOS surface station, has been used in this installation.

The air inlet has been placed on top of the mast on the upper floor of the boat, in front of the main exhaust of the vessel and connected to the multi position valve through Dekabon tubing (Synflex 1300, ¼ inch). The GPS system has also been installed on the main deck (Figure 14). The meteorological sensors providing information on temperature, pressure, relative humidity, wind speed and direction are placed opposite to the GPS system on the same platform.

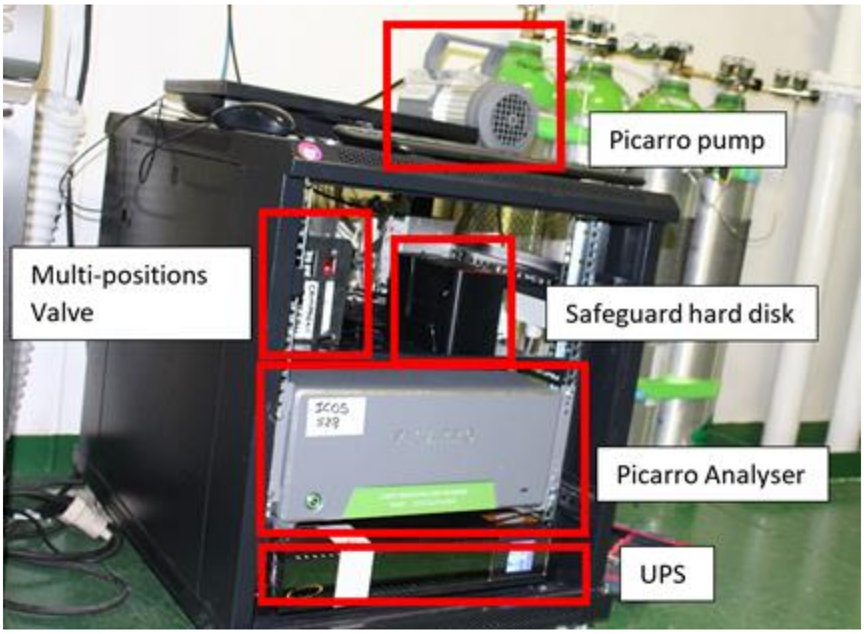

Figure 13: *Instrumental set up on the SOOP COLIBRI.*

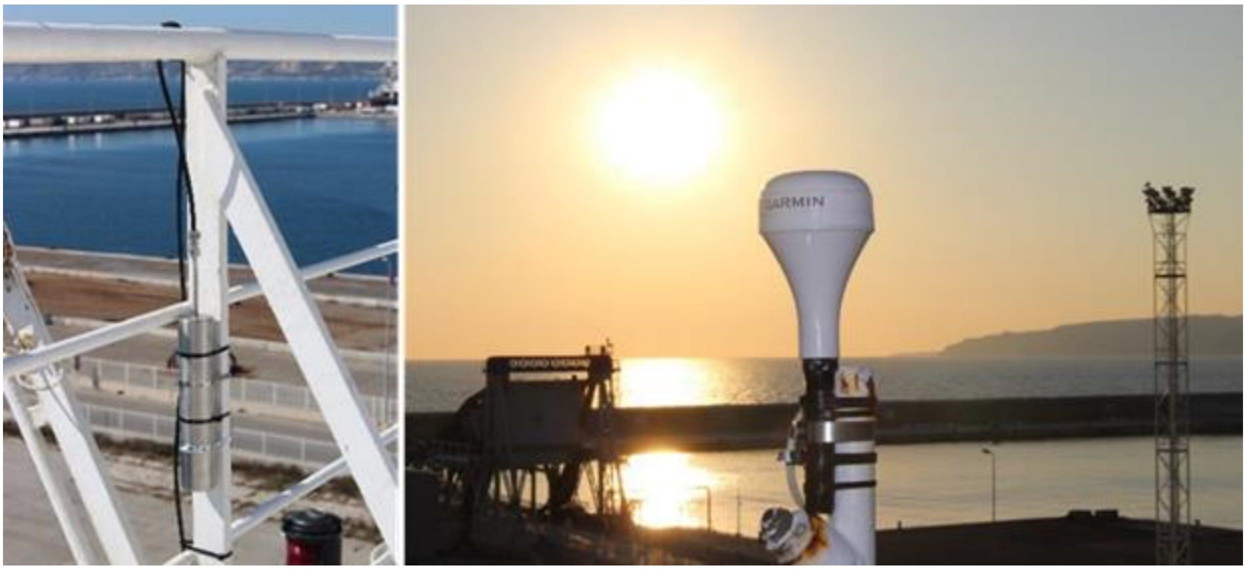

Figure 14: *Air inlet (left) and GPS sensor (right).*

<u>System test and validation :</u>

The equipment has been first tested and assembled at ATC, following protocols used for all ICOS atmospheric analysers in order to characterize the measurement repeatability, and the sensitivity to different parameters (water vapor, content, atmospheric temperature and pressure, etc…). Due to the delay to get the authorisation of installation on board COLIBRI, the system was used during the intensive scientific campaign AQABA across Mediterranean and around the Arabian Peninsula (May - June 2018), on board the Kommandor Iona vessel. On this campaign, the use of the data, amended by additional air-quality measurements, was used to assess the air pollution caused by marine traffic in the research area (Celik et al., 2020). The setup of the monitoring system onboard the SOOP COLIBRI was realized in early

March 2019 in Marseille, enabling first data acquisition starting from March 19th 2019. The first two months the vessel was quayside which enabled us to test our instrumentation setting, resulting in a first upgrade of the GPS acquisition system interface that was done in May 2019. The GPS data acquisition occurring every second, initially piloted by the Picarro computer, was interfering with the Picarro G2401. In June 2019, the vessel started its first trans-Atlantic cruise, followed by a second one in late August, beginning of September. The first data were recovered in mid-September when the vessel came back to France. In November 2019, a second upgrade of the GPS acquisition system was implemented, as well as an automatic data transfer system activated every time the boat reaches a harbour. A 4G router has been implemented into the instrumental rack, and an automated routine (ICOS Station) developed at ICOS ATC enables automatic data transfer to the ICOS ATC database. With this system we are also able to remotely connect and pilot the instrument while the vessel is at quay. Since the end of March 2019 the monitoring system has then been running continuously, and the data from the SOOP COLIBRI are integrated and processed in the ICOS database.

Measurement protocol :

The GHG analyser onboard the SOOP COLIBRI is running continuously, independent of the location of the ship. The measurement protocol is quite similar to the one used for the ICOS atmospheric stations. A suite of three cylinders (Table 6) is used to calibrate the instrument every 30 days, and a quality control tank (so called target tank) is analysed for 20 minutes every 8 hours. The calibration procedure consists of 30 minutes measurements of each of the calibration cylinders, reproduced four times. The evaluation of the calibration sequences is done automatically, based on the standard deviations of the raw measurements, the minute averages, and the injection averages (Hazan et al., 2016). The regular measurements of the target gas show very good performances of the measurements with biases lower than 0.05 ppm for CO_2 and 0.5 ppb for CH_4 from March to September 2019, when work was done on the vessel near the analyser. Then we observed an increase of the biases up to 0.15 ppm and 0.3 ppb for CO_2 and CH_4 respectively. A small leakage on the pressure regulator used for the target gas cylinder was found during an inspection done in July 2020, indicating that the bias was not affecting the ambient air measurements but only the target gas measurements. See also Table 3 for performance on the target measurements.

Cylinder ID	CO_2 (µmol/mol)	CH_4 (ppb)	CO (ppb)
CAL 1	386.34	1794.64	76.25
CAL 2	409.15	1947.13	153.70
CAL 3	448.38	2088.61	286.66
Target Gas	403.67	1962.70	135.97

Table 6: *Calibration and target cylinders used onboard SOOP COLIBRI.*

Data quality assessment and comparison to the CAMS forecast product

As discussed in Section 2.2.1.3, the regular analysis of a target gas indicates for SOOP COLIBRI an excellent measurement repeatability under flawless operation (Table 3). However, the first year of measurement indicates the precautions that must be taken to avoid the appearance of leaks, possibly linked to the vibrations of the ship, and the importance of using calibration and target gases supplied by the ICOS/CAL. Unlike the case of TAVASTLAND, the COLIBRI ship does not pass near an ICOS station that would allow a side-by-side comparison.

On the other hand we have compared the COLIBRI measurements with the CO_2 and CH_4 high resolution forecasts performed by the Copernicus CAMS. Three examples are shown in Figure 15. The CAMS experiments have systematic biases for CO_2 and CH_4, generally on the order of 1%, which are well documented with the trimestral validation reports using the ICOS surface station and TCCON/NDACC total column measurements (Schulz et al., 2020). The comparison with the COLIBRI observations brings interesting information about the performance of the CAMS experiment to reproduce the latitudinal gradient and the frontal system crossing the Atlantic Ocean. The Aug./Sept. transect (red curves, left side) shows that the model reproduces the North/South gradient correctly, as well as the day to day variabilities of CO_2 and CH_4 (with one exception for a CH_4 increase in the simulation at 18°N). The position of the ITCZ, around 10°N is well simulated, however the amplitude of the CO_2 jump when crossing this zone remains underestimated. The second example in May-June 2019 (green lines, middle) is interesting. For CH_4 it appears that the model overestimates the North/South gradient, with a larger disagreement at low latitudes, and for CO_2 the model shows an increase of 2 ppm in mid-latitudes, when COLIBRI data display a 1 ppm decrease at the same latitudes. This feature indicates that the carbon uptake season is starting too late in the model. The plume of continental air masses through the Atlantic is probably correctly represented, but the ecosystem model does not have the correct seasonal phase. Then the third example on Nov.-Dec. 2019 (blue curves, right side) shows a strange 4 ppm CO_2 decrease at 22°N. This event corresponds in fact to a reinitialization of the CAMS experiment which occurred on Dec. 1st 2019. Of course this comparison does not assess the quality of the observations, but rather those of the CAMS simulations. However, the consistency of short-term variations in the observations and the CAMS experiments also indicates that the measurements are for example not highly contaminated by the ship's stack which would not be reproduced by the model.

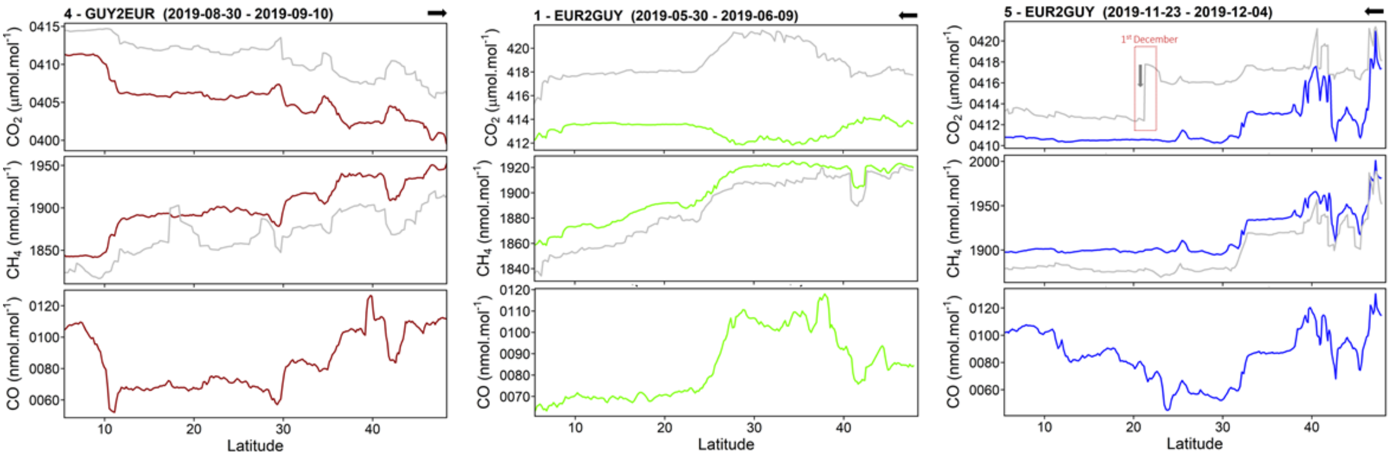

Figure 15: Comparison of CO_2 (upper panels), CH_4 (middle panels) and CO (low panels) measurements *on board SOOP COLIBRI (coloured lines) with the high resolution forecast of the CAMS model (grey lines) for three transects between French Guiana and Europe.*

3.3.3 Installation on SOOP ATLANTIC SAIL

The M/V ATLANTIC SAIL (Atlantic Container Lines, ACL; Figure 16) is a combined car and container vessel operating on a service between North America and Europe. The first port calls on both sides of the Atlantic are Liverpool, UK, and Halifax, Canada (Figure 17). It also covers part of the European shelf as the ship also serves the port of Hamburg, Germany.

Figure 16: North Atlantic SOOP line ATLANTIC SAIL (photo is courtesy of Atlantic Container Lines).

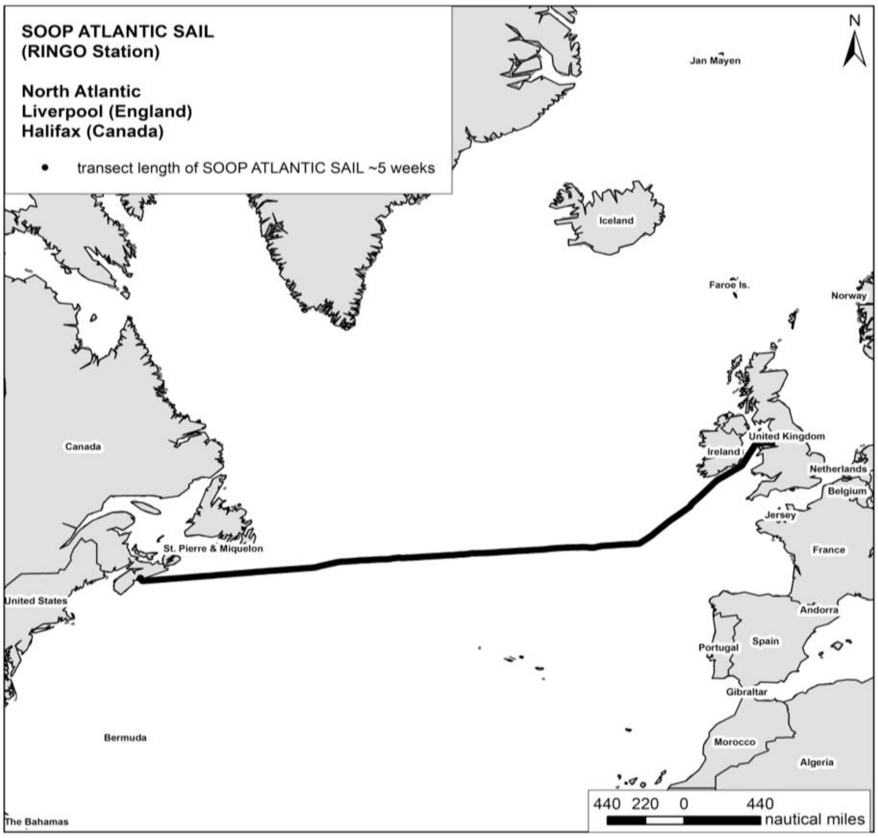

Figure 17: Single transect across the Atlantic of SOOP ATLANTIC SAIL (IMO: 9670585)), a RO/RO Container carrier.

The SOOP line between Europe and North America has been operated since 2002 by GEOMAR with different ships. Since 2005 the pCO_2 installation has been on board an ACL vessel. In 2018 the installation was moved from the old ship (ATLANTIC CARTIER) to the ATLANTIC SAIL. The main instrumentation (General Oceanics pCO_2 system 8050, GO system) is installed in the engine room, where fresh seawater is drawn from the lower sea chest at approximately 10 m water depth. Atmospheric air is drawn from outside through an 80 m long Dekabon tubing. The air inlet is located on the top of the housing for the exhaust at approximately 35 m height. This was the only position that could be reached from the engine room. Even if the position is not optimal, clean air can reach the inlet. A weather station with wind speed and wind direction is installed next to the inlet so that unfavourable wind directions can be filtered.

The CO_2 measurements for sea surface pCO_2 are done using a LI-COR infra-red CO_2 sensor (LI7000). These sensors have proven to measure the xCO_2 in seawater applications to ±0.2 ppm, which basically determined the target accuracy for the MBL measurements by the SOCONET initiative (Wanninkhof et al., 2019). To improve the measurement uncertainty of the xCO_2 measurements it was planned to exchange the LI7000 with a Picarro sensor (G2131-i). Since the sensor was also used for xCO_2 measurements in air that was in equilibrium with seawater we had massive problems with the vacuum pump of the Picarro instrument and the exchange of the pump membranes was not a task that could be easily done on board. Therefore, we decided against this analyser. In 2019 first laboratory tests with a new CO_2 sensor (LI-COR LI7815) were performed. The integration of the LI7815 into the existing GO system seemed to be straightforward and the first tests showed promising results that need to be further evaluated in the field. There are groups at NOAA (Miami, USA) and CSIRO (Hobart, Australia) that also work on the integration of the LI7815 and new design of the whole GO system to better work with the LI7815. Thus, it is very likely that the LI7815 becomes the new standard for oceanic pCO_2 measurements. Other benefits are the price and the maintenance (all parts of the instrument - optical bench, pump, batteries, internal computer - can be exchanged by the user during port call). The new LI7815 can be easily swapped between installations which is a huge advantage as the time for servicing the installation on board the vessels is often limited due to short port calls.

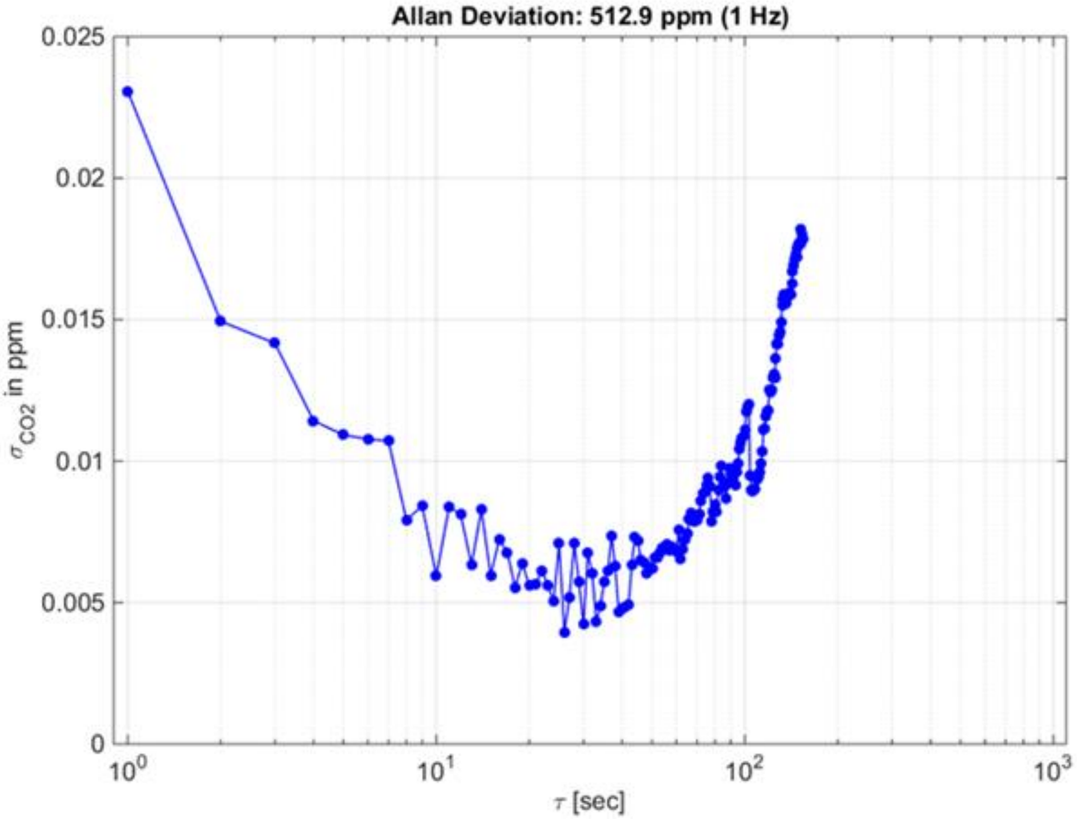

Figure 18*: Allan deviation analysis of standard gas (512.9 ppm CO_2) measurement with the LI7815. Measurements were recorded at 1Hz.*

The Allan plot in Figure 18 shows that, for an averaging time of 10 seconds, the repeatability is better than 0.01 ppm CO_2. Towards long averaging times, the repeatability gets worse due to the increasing impact of long-term drift. Thus, we decided to average the measurements for 20 seconds. The GO system reports a data point approximately every minute and the last 20 seconds before reporting are used for averaging. However, the 1Hz raw data are always available, too, so that a reprocessing of the data is always possible. Together with its high precision it makes this sensor a suitable candidate for the combined approach onboard vessels like the SOOP ATLANTIC SAIL. However, after operating for some month onboard the ATLANTIC SAIL, several problems occurred with the new sensor:

1. The GO system was designed for gas flows of around 100 mL/min, but the LI7815 operates with 250 mL/min. Even if the equilibration looked fine, it happened that water droplets were sucked into the gas lines. This caused clogging due to the buildup of salt crystals.
2. The software of the GO system needs to get changed due to the new flow characteristics of the LI7815. This is possible, but needs engineering time.

Both points caused the system to stop several times. The reasons for stopping were always clear, but the LI7815 was removed from board until the necessary software changes were done. However, when the system was running it could be seen that the measurement precision was improved. The exact quantification needs more time. But the field test also indicates that the calibration interval can be extended without a loss in data quality. The calibration data showed a drift of 0.005 ppm/d.

Figure 19 shows the GO pCO_2 system on board the M/V ATLANTIC SAIL. The system is commercially available and is used by many groups around the world. The system was designed for the use of a classical infra-red detector from LI-COR (LI6262 or LI7000). As mentioned above, in order to improve the precision of the atmospheric measurements a different detector should be installed. The approach onboard the M/V ATLANTIC SAIL was to use the same instrumentation that is used for seawater pCO_2 measurements also for accurate atmospheric xCO_2 measurements. During a cruise in 2017 it was found out that using filter wool (like it is used in regular kitchen hoods) in the air inlet improved the stability of the measurements.

This might be due to the effect that salt crystals are kept out of the air tubing. Salt crystals might have an effect on the water vapor in the air line depending on its temperature. However, air is constantly pumped through the long tubing to ensure that the line is always well flushed. The whole system is set up in a way that it runs several standard gases followed by 10 minutes of atmospheric air before it measures seawater pCO_2 for three hours. Then the cycle starts again so that atmospheric air is measured approximately every 4 hours during the Atlantic crossing. When the system switches to atmospheric air the air is dried using a Peltier cooler that operates between 2°C and 5°C and using a Nafion dryer afterwards. Then the air is directed to the CO_2 sensor. The current setup onboard the SOOP ATLANTIC SAIL is illustrated in the lower part of Figure 19.

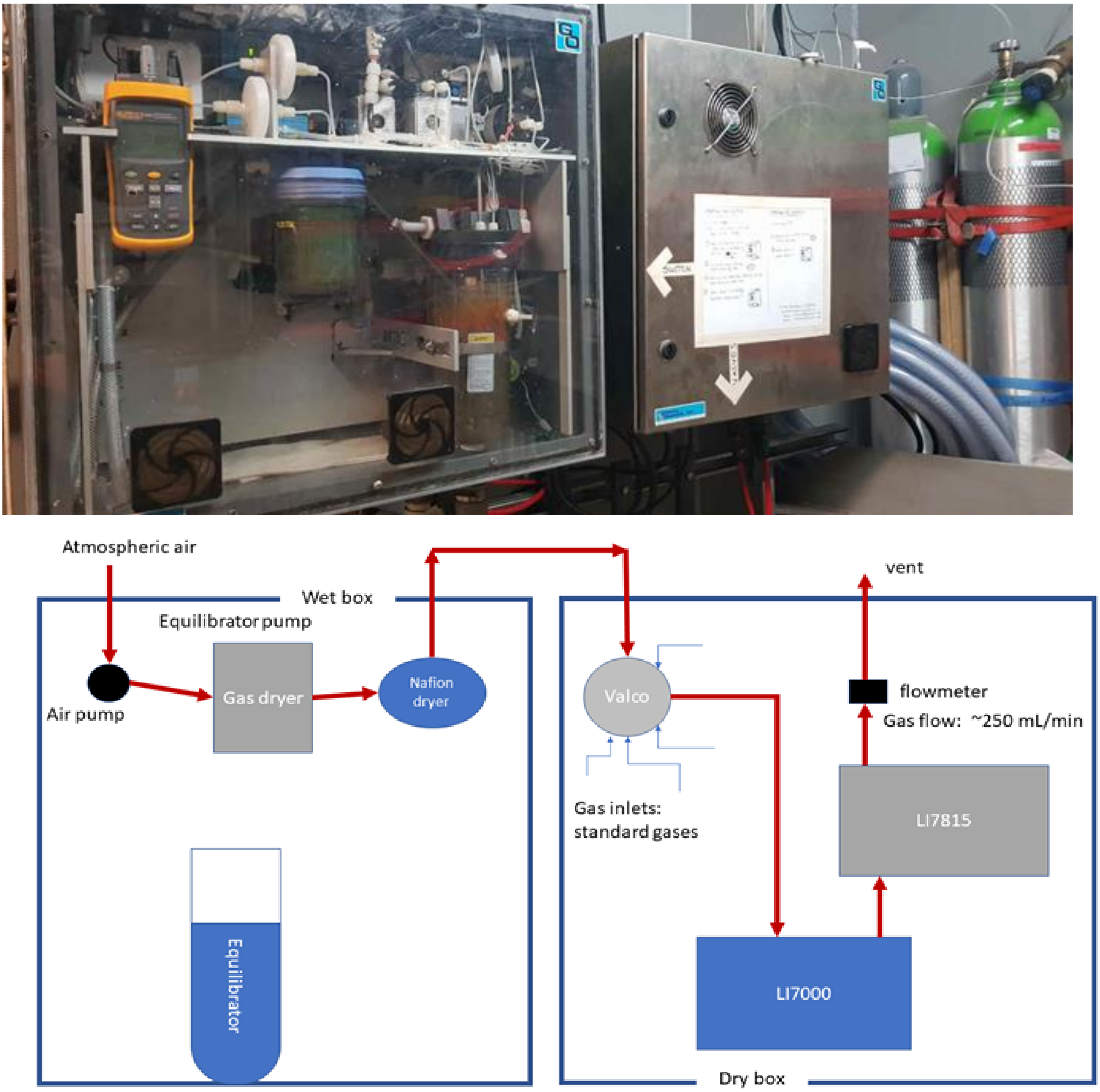

__Figure 19:__ Photo and schematic of the GO system used onboard SOOP ATLANTIC SAIL. The upper photo shows the so-called "wet box on the left where the seawater equilibration takes place. Also the pumps and drying units are located in the wet box. The "dry box" to the right contains a Valco multi-position valve and the CO_2 sensors. In the background one can see the gas bottles with standard gases. The lower schematic shows the gas flow of atmospheric air. The air tube is directly connected to the dry box where constantly air is pumped from the inlet. The air is dried with a Peltier cooler and Nafion tubes. The dried air goes via the Valco valve to the CO_2 sensors.

Data evaluation

Due to the change of the carrier, long subsequent ship yard time, and limited access to the ship in the last phase of the project due to the Covid 19 pandemic, a final evaluation of the accuracy of atmospheric CO_2 measurements using a system designed for pCO_2 measurements for short intervals cannot be evaluated within this RINGO project time frame. However, first results (Figure 20) using an NDIR sensor (Licor LI7000) shows the potential of the setup. In addition, a better shielding of the inlet line against water and salt intrusions, the use of at least one additional standard and a target gas with a CO_2 concentration close to ambient air, are definitely suited to increase the accuracy of the air measurements. With the steps towards improvement of the system and following the recommendations listed in Section 2.2.2, it was possible to achieve atmospheric CO_2 measurements with a repeatability of ±0.1 ppm.

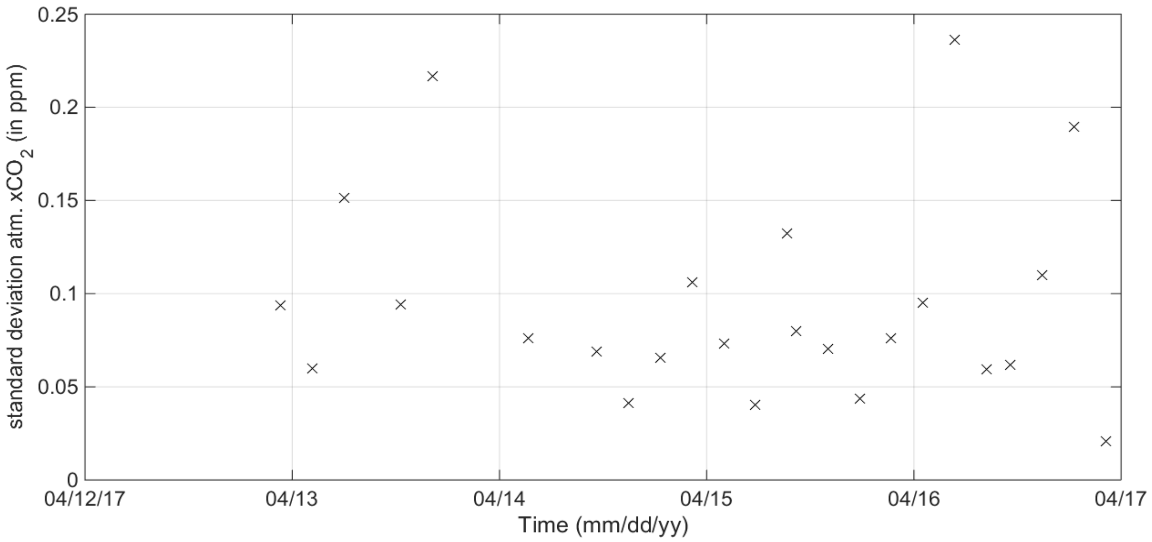

***Figure 20:** Standard deviation from atmospheric xCO_2 measurements with a GO instrument during a North Atlantic crossing. The data were recorded using an NDIR sensor (Licor LI7000) in April 2017. During the interval of atmospheric air measurement the data were recorded every minute. Only intervals with at least 5 data points were used for averaging. 70% of the data have a standard deviation better than 0.1 ppm.*

The superior accuracy and long-term stability of CEAS instrumentation relative to the currently mostly used LI-COR 7000 NDIR sensor has shown the potential for large improvement of the atmospheric air measurements in this "dual use" mode (Figure 18). However, a complete assessment of the performance in optimized configuration between the pCO_2 seawater unit and these sensors, including regular test runs of a target gas and postprocessing by the ATC, is not finalized.

4 CONCLUSIONS AND OUTLOOK

We conclude that it is possible to install systems for ATC-conform measurements of CO_2, CH_4, and CO on SOOPs, allowing to benefit from the fact that the platforms need to be visited for maintenance purposes due to the OTC-installation anyhow, and to retrieve data with a unique spatiotemporal coverage from areas from which data cannot be gathered by other means. Due to unforeseeable delays due to i.e. Covid 19, the long-term operational evaluation could not be finalized during the RINGO project time line, but the necessary steps will be pursued further. Though not finally evaluated, the already available data suggest that sporadic measurements of atmospheric CO_2 mole fractions close to ATC standards can be achieved using existing measurement infrastructure for pCO_2 measurements, if additional steps are taken to enhance the quality of these measurements, which is described in this report. It was possible to establish the required solutions for handling of these data at the ATC, which should simplify the integration of additional systems if this is decided within the ICOS consortium.

Some obvious next steps and items to be resolved have been identified. Contamination from the vessel could potentially be further minimized by a 2nd inlet system at the stern of the ship, using relative wind direction as an indicator for strong tail winds and criterion for switching of the inlet. Operational implementation of back-trajectories could be implemented at the ATC to facilitate interpretation of the data. Assuming that based on final evaluation, the "dual use" of OTC pCO_2 instrumentation for atmospheric measurements should be pursued further on some of the ICOS SOOP lines, the responsibilities of OTC and ATC have to be clarified and coordinated. The data is of value for both communities. Handling by the ATC appears most logical, but as the instrumentation for pCO_2 on ICOS (OTC) lines is not streamlined, the unification of data formats and postprocessing reached for ATC-conform instrumentation might not be achievable.

The regular atmospheric data from the ship lines considered here are expected to be an important extension of the ICOS atmospheric network. When estimating spatio-temporal CO_2 flux fields for Europe by (regional) atmospheric inversions, these data can be used as additional "stations", just in the same way as the data from fixed ICOS stations. As the ship tracks encircle the main European land masses, they will greatly help to constrain the inflow boundary condition of the atmospheric inversions. Up to now, air crossing the western inflow boundary of the spatial domains of the regional inversions is sampled inside the continent for the first time. The additional sampling of the air just before it enters the continent will reduce uncertainties of CO_2 flux estimates especially for western and south-western Europe. In addition, data from the cross-Atlantic leg of SOOP COLIBRI will help to constrain the oceanic CO_2 exchange and its variability.

Finally, we would like to emphasize that the work performed within this Task 3.2 of RINGO unambiguously demonstrates the added value of using the combined and complimentary expertise of different thematic branches within the ICOS RI. Finding ways to promote cross-national and cross-domain work within the ICOS RI is a prerequisite to fully exploit its scientific potential.

5 DEFINITIONS, ACRONYMS AND ABBREVIATIONS

ACL	Atlantic Container Line (ship owner/operator)
ATC	Atmospheric Thematic Center
Copernicus	The European Union's Earth Observation Program
CAMS	Copernicus Atmosphere Monitoring Service
CEAS	Cavity Enhanced Absorption Spectroscopy
ESRL	Earth System Research Laboratories
EUROGOOS	European Global Ocean Observing System
GAW	Global Atmosphere Watch
GEOMAR	Helmholtz Centre for Ocean Research Kiel
GO system	General Oceanics pCO_2 system 8050.
GPS	Global Positioning System
ICOS	Integrated Carbon Observation System
ICOS HO	Integrated Carbon Observation System Head Office
IOW	Leibniz Institute for Baltic Sea Research Warnemünde
ITCZ	Inter Tropical Convergence Zone.
KVM	Keyboard Video Mouse
MBL	Marine Boundary Layer
MSA	Monitoring Station Assemblies for ICOS ERIC Member countries' Atmosphere station, Ecosystem station and Ocean station networks
NDIR	Non Dispersive Infra Red sensor
NDACC	Network for the Detection of Atmospheric Composition Change
NOAA	National Oceanic and Atmospheric Administration
OSSE	observation system simulation experiments
OTC	Ocean Thematic Center
pCO_2	Partial pressure of CO_2
RO/RO	Roll-on/roll-off (RORO or ro-ro) ships are cargo ships designed to carry wheeled cargo, such as cars, trucks, semi-trailer trucks, trailers, and railroad cars
RoU	Reduction of Uncertainty
SMHI	The Swedish Meteorological and Hydrological Institute
SOCAT	Surface Ocean CO_2 Atlas (SOCAT)
SOOP	Ship of opportunity
TCCON	Total Column Carbon Observation Network
UPS	Uninterruptible Power Supply
UVSQ	Université de Versailles Saint-Quentin-en-Yvelines
WMO	World Meteorological Organization

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7 Appendices

<u>A1: Rudimentary parts list for TAVASTLAND setup (see Figure x in chapter *3.3. 1 Installation on SOOP*)</u>

19” Rack: coated steel (with removable walls and roof!); different suppliers

CO_2 sensor: PICARRO G2401 with vacuum pump (Vacuubrand MD-1); procured by ICOS HO

Steel tubing: SS 1/8” Swagelok, thick-walled, 0.035”, 6mm steel pipe, Swagelok

Air line: Synflex 1300 (aka Decabon), 8 mm, 6mm; different suppliers

Gas cylinder: Luxfer L6X, 20l/WP 200, CGA590, Luxfer, provided by ATC CAL

Two-stage regulator: TESCOM 64-3460KA412 HST, PCTFE valve seat (!), CGA590; TESCOM

Multiposition valve: VICI VALCO 724EMT2SD8MWMHC; VICI

Solenoid valve: Parker Series 9, 009-0207-900, 3-way, First Sensor

Airpipe flushing pump: 617CD32, WOB-L Piston; Gardner Denver Thomas

Mass flow controller: Bronkhorst 6300er series; Bronkhorst

Mass flow meter: Bronkhorst 6300 series; Bronkhorst

Absolute pressure transmitter: OMEGA Newport PAA33X-C series; OMEGA

Air cooler (condenser): Bühler TC Standard 6112, adjustable automatic temperature control, condensate pump; Bühler Technologies

UPS: Riello SDH 3000-5 (the UPS shall have Remote Emergency Power Off, REPO ability!); Riello

Laptop USB KVM console Crash Cart Adapter CV211; ATEN

RS232-USB Adapter; Meilhaus

Laptop; different suppliers

Control Unit: NI-USB 6221 module; National Instruments

Liquid water guard & alarm: sensors (KS3, LA25s) and electronics (LA1.4, FA1.4); M&C Tech group

Time server & GPS: Meinberg M200 with GPSANT HF2020; Meinberg

Weather shield: ATC self-built model; by courtesy of ATC

Air line heating: QUINTEX

Switch boxes & electrical installation parts and material; different suppliers