Berichte
zur Polar- und Meeresforschung

Reports on Polar and Marine Research

The Expedition of the Research Vessel "Polarstern" to the Antarctic in 2012 (ANT-XXIX/1)

Preliminary extract

Sea Trials and Data Comparison of pCO_2 Measurements in Air and in Seawater Obtained by two Different Systems on Board RV "Polarstern" during ANT-XXIX/1 (27.10.2012 – 27.11.2012)

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Introduction

The level of atmospheric carbon dioxide (CO_2) has been continuously rising due to fossil fuel burning. As CO_2 is a significant greenhouse gas, this may have implications for the radiation balance of the Earth and thus for global climate. In the oceans, the CO_2 content has increased due to air-sea exchange of the gas, partly mitigating the CO_2 increase in the atmosphere. It is vital to know how much CO_2 is taken up by the oceans, what factors determine the uptake, whether there are feedback effects and what the inter-annual variability of this uptake is. Part of these questions can be tackled by measurements of CO_2 in the surface ocean at as much as possible places and all through the year (since CO_2 in the surface layer of the ocean is involved in a seasonal cycle posed by temperature changes and biological activity). Another part can only be done through a modelling effort, where, however, the measured data form the backbone of those models.

A global community of CO_2 researchers is running pCO_2 (partial pressure of CO_2) measurements in the ocean and the atmosphere for getting a hold on the exchange of the gas between ocean and atmosphere. Measurements have started in the 1960s already and the frequency of the data obtained has very strongly increased. Recently, 6.3 millions data points have been published as a quality controlled consistent data base as part of the SOCAT (Surface Ocean CO_2 Atlas) project; Hoppema is involved in this effort. The data base also contains data collected previously with FS Polarstern. SOCAT is updated regularly; the next version will contain many data from the GO pCO_2 system that is permanently installed on board. Since FS Polarstern sails to ocean provinces (the polar regions) that are not often visited by other ships because of limited accessibility, it will contribute rare and most valuable data to this major data base.

Used technology

a) GO system:

The GO (General Oceanics) pCO_2 system is a much used pCO_2 system on ships of opportunity (generally dubbed VOS – Volunteer Observing Ships). It has been on FS Polarstern since 2007. The system uses an equilibrator chamber to bring surface sea water, drawn from the ship's pump, in equilibrium with a headspace gas (air) by continuously spraying the water in via a spiral nozzle (Fig. 1 and Fig. 2). The headspace gas is circulated and dried within the system and then pumped to the built-in Li-cor Infrared CO_2 Analyzer for detection of the CO_2 concentration. Alternatively, marine air is pumped down to the lab and circulated in the GO system for detection of its CO_2 concentration. The system is calibrated every few hours with 3 reference gases with CO_2 concentrations of about 200, 400 and 600 ppm, and

nitrogen. Within the CO_2 community the GO system is the unofficial standard system for underway CO_2 data.

Fig. 1: GO system part I, gas preparation (Image from GO user manual)

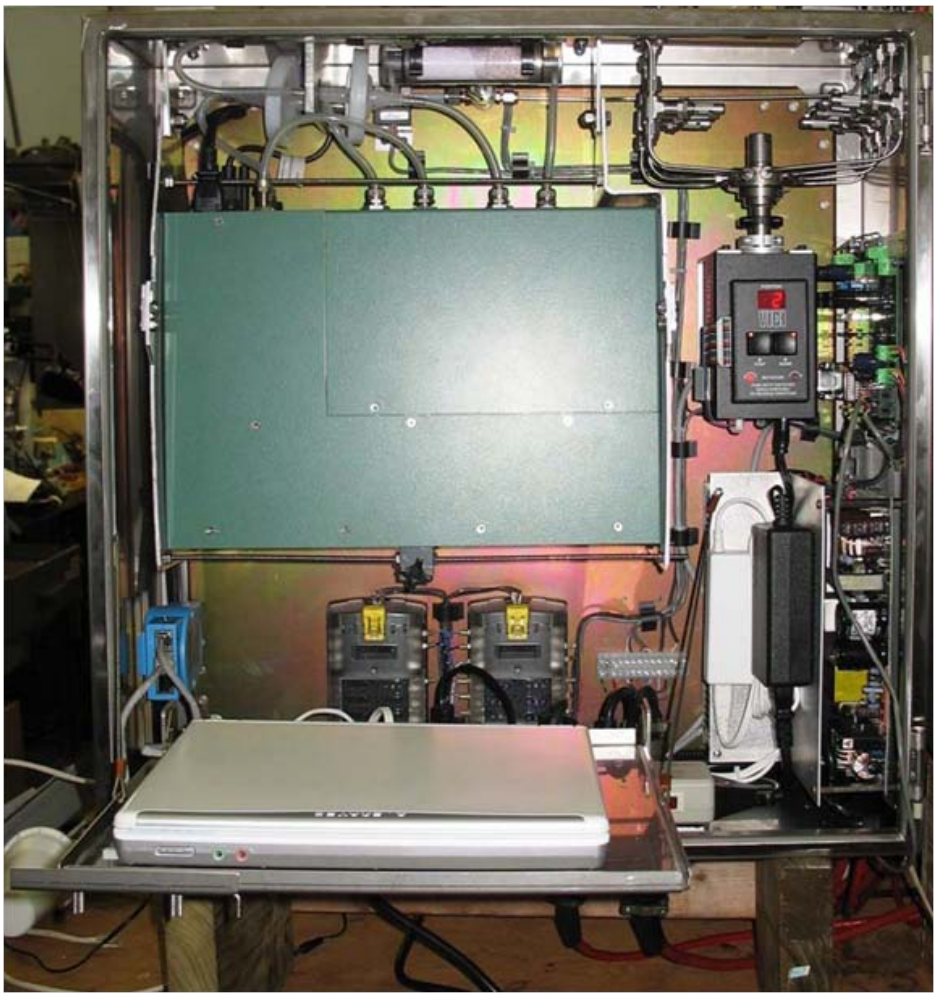

Fig. 2: GO system part II, gas analyser (Image from GO user manual)

b) SubCtech System “OceanPack”:

The SubCtech “OceanPack” system is small, robust and designed as “ready to use” for underway pCO_2 measurements in water and in the atmosphere. CO2 is drawn from the seawater flow via a membrane system; a specially adapted LI-COR® analyzer fully integrated with real-time processing with up to 1 Hz raw sample rate provides on-line retrieved pCO_2 values.
The basic design includes two separated and independent systems for pCO_2 measurements, one for air (Fig. 3) and the other for water (Fig. 4).
Calibration of the systems is done automatically by zeroing without need for external reference gases. Calibration using reference gases can be optionally implemented.

The main features of the system are:

- High accuracy due to automatic H_2O, temperature and pressure compensation.

- Robust, versatile and compact housing for marine applications. Complete and easy to maintain “underway” system.

- Easy handling and intuitive overall design: e.g. red and green signal lights, only one start and stop button to operate the whole system
- Already includes the LI-COR® pCO_2 sensor, based on the LI-840 or LI-7200 family, developed for high-precision atmospheric measurements, adapted to sea-air exchange analyzing systems.

- Permanently checked with internal auto calibration (zeroing) or optionally span standard gases.

- Expandable by easy integration of instrumentation through the SmartDI® Datalogger, e.g. Optode, TriOS, Turner, Wetlabs Fluorometer or Turbidity sensors, Seabird or Sea&Sun CTD and Thermosalinograph, Water-Sampler, Nutrient Analysers and RS-485 Bus e.g. for valves.

- Independent air-CO_2 analysis with the Top-Box, which consists of the excellent LI-7200X analyzer, optionally “Arctic Version” with heating and water-proof Air- Intake Box. Only one data link to the OceanPack Datalogger is required, no tubes.

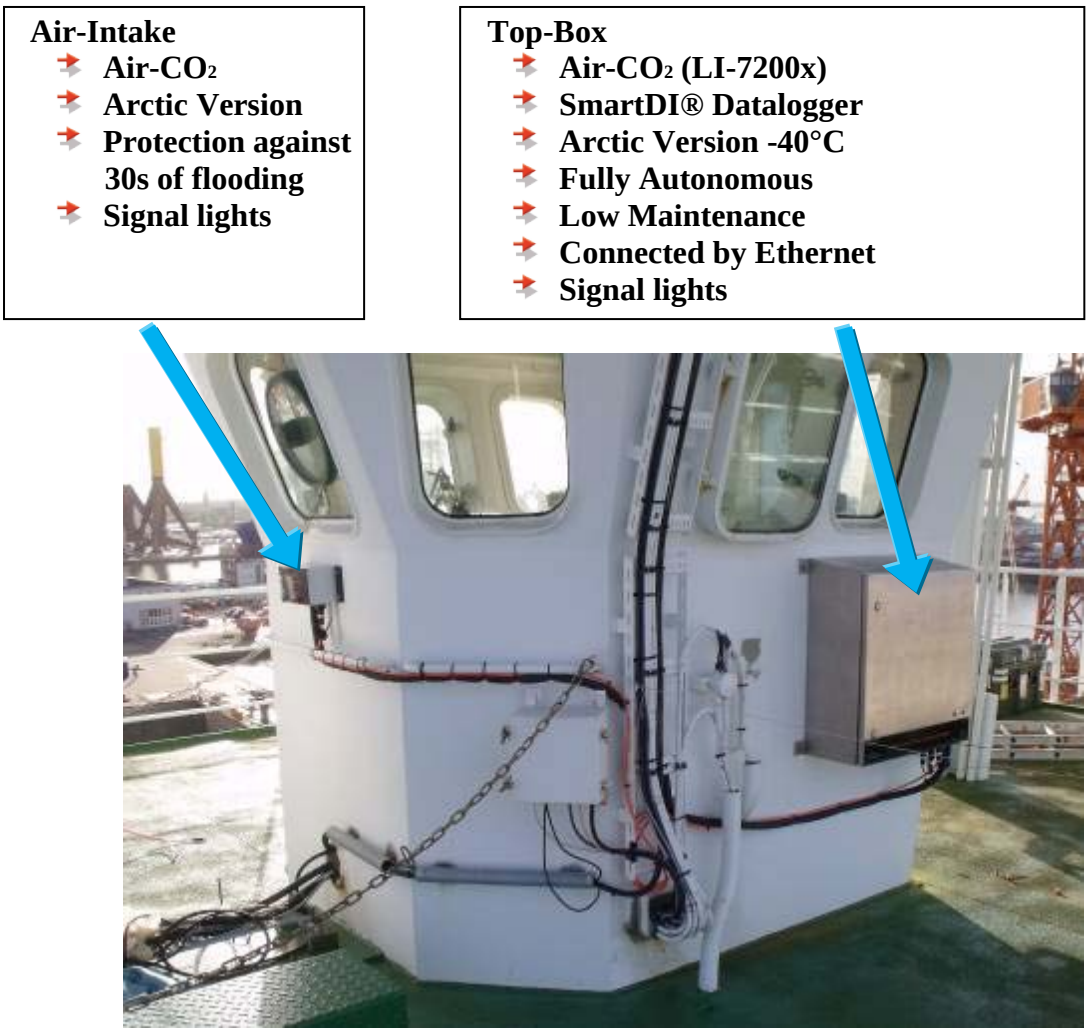

Fig. 3: SubCtech Top-Box for Air-CO_2 underway measurements on RV “Polarstern”

Fig. 4: SubCtech "Ocean Pack" for Water-pCO2 underway measurements on RV "Polarstern", (Images SubCTech)

Objectives

pCO_2 measurements in air and seawater are carried out since more than five years on board of RV „Polarstern" using a General Oceanics system (GO). Although the GO system has been designed to be run autonomously, the technical complexity combined with frequent defect parts of the system has made the running of the GO system cumbersome. This has led us to look for alternative systems. After a demonstration of a new system by the company SubCtech,the "OceanPack" system was installed in October 2012 on board Polarstern in parallel to the existing GO system and tested during ANT-XXIX/1 (27.10.2012 – 27.11.2012) on the way between Bremerhaven and Cape Town.
The main objectives of this campaign were testing the functionality of the SubCtech system under real sea conditions and to compare the output of both systems to assess the reliability of the new system.

Work at Sea

After the installation of the OceanPack system in Bremerhaven, a complete functional test could not be carried out, due to the lack of regular seawater at harbour. Complete and successful tests were carried out at high sea including all water connections, pipe, water flow, communications, data input and data output.
Both systems were started for real pCO_2 measurements on 30.10.2012 and stopped on 26.11.2012.
Complete data of each system and additional navigational and environmental data were collected every three days and sent to land for evaluation. Preliminary results were checked, discussed and sent back to the ship for farther tuning and check of system parameters.
Finally, all data of the comparison campaign were processed.

Preliminary results

Data of GO system were processed using a special algorithm and software, due to the fact that the GO system is not able to provide retrieved pCO_2 values directly.
The OceanPack system is providing the retrieved pCO_2 values directly and in addition all other environmental and navigation data needed.
The OceanPack system is easy to use and works automatically without extensive interaction or controlling needed by technical staff.

The GO system was running excellently. Only criticism is that the EQU and ATM gas flows were not perfectly dried, but this is not critical as the system corrects for this.
The OceanPack system was also running in a stable way. Its data file is remarkably complete, containing a plethora of housekeeping and troubleshooting data as well as raw and calculated results. This certainly is much more user friendly than the GO output. Additionally, no data processing, whatsoever is here needed, except lining up with Ship's Data Acquisition System (DSHIP) for geographical positions. That makes it fabulously easy to use.
The OceanPack instrument is NMEA compatible as delivered, which, together with the on-board calculation of pCO_2, make integration with DSHIP straightforward.

Fig. 5 presents the resulting overview of data comparison of both pCO_2 systems.

The following coincidences and differences were found:

- OceanPack ocean data were 'delayed' in time by about 25 minutes compared to the GO data caused by bad clock on one of the instruments. No reduced temporal resolution is evident (i.e., it does not appear to be caused by a 'slow membrane').

- OceanPack atmospheric pCO_2 is systematically ~4 ppm lower than that of the GO system, probably due to miscalibration of the OceanPack system.

- OceanPack and GO seawater pCO_2 matches fairly around 370 ppm, but OceanPack data grows progressively higher at high pCO_2. The regression between them is not very good: SCT=1.18*GO-65 (or, alternatively stated, in

order to correct the OceanPack data (SCT), use: SCTcorrected = SCTraw*0.832+61.2). After performing latter correction, the RMSE of differences between GO and SCT is 3.5 ppm, which is acceptable, especially because the GO system appears rather noisy. After this correction, the likeliness between the two instruments is remarkable.

- Preliminary judgement: Precision and stability of the OceanPack instrument appear to be excellent. However, a severe miscalibration currently means that data are useless for scientific use. Correct calibration using reference gases are an option in the OceanPack system and should be implemented soon.

- If SubCtech can convince the scientific community that OceanPack system can demonstrably maintain its accuracy over long periods of time, the instrument is deemed to be operationally superior to the currently employed GO system from “General Oceanics”, which is very high quality, but troublesome to operate and maintain.

Conclusions:

Comparison of results of the two pCO_2 systems (GO and SubCtech) on board RV “Polarstern” during ANT-XXIX/1 shows that the SubCtech system has a very good performance, except for the gradual but significant drift and general inaccuracy, both likely due to lack of regular calibrations with reference gases. The basic OceanPack system is including the calibration with reference gases as option. This will be later installed and tested on “Polarstern”. It should be stressed that for the purposes that we are using the oceanic pCO_2 data (i.e., within the global pCO_2 community), the calibration with reference gases is obligatory and cannot be done without. The SubCtech system can only compete with the GO system when appropriate calibration is performed.
In the atmospheric data the inaccuracy is seen as an offset between instruments between 4 and 6 ppm.
The difference in the oceanic signal is much more noisy, due to the 'jumpiness' of the GO signal, which the OceanPack system does not exhibit. Generally the signal from the OceanPack system (after applying the earlier mentioned linear correction to best match the GO signal) very well resembles the GO system. The mean±standard deviation difference is -0.1±3.0 uatm.
SubCtech is recommended to implement the calibration procedures in the OceanPack system as soon as possible.
The scientific community is asked to continue monitoring and comparison of the two instruments during the coming expeditions of RV “Polarstern”.

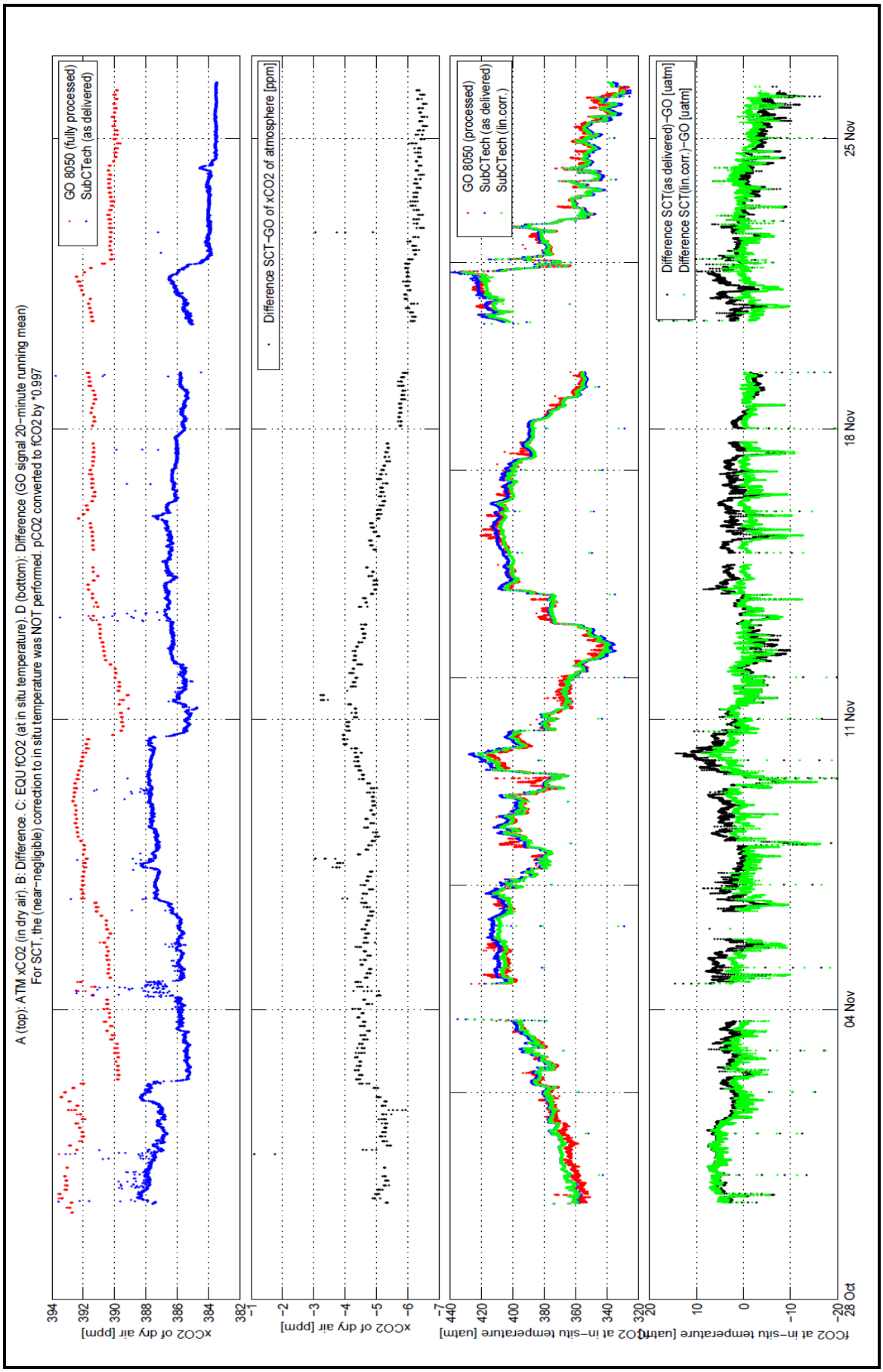

Fig. 6: Overview of comparison results of both pCO2 systems (GO and SubCtech, SCT) on board RV" Polarstern" during ANT-XXIX/1