Work Package 11
Optimisation of ocean observing capability

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Cross-over analysis of parameters between platforms

Lead beneficiary: ULPGC

Lead author: Melchor González-Dávila (melchor.gonzalez@ulpgc.es)
Contributors: Siv K. Lauvset, Laurent Coppola, Ute Schuster, Melchor Gonzalez (UiB, CNRS, UNEXE, ULPGC)

Work Package leader: Ute Schuster (UNEXE, u.schuster@exeter.ac.uk)

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Contents
EXECUTIVE SUMMARY ................................................................................................................................................. 3
1. INTRODUCTION ......................................................................................................................................................... 4
   1.1. Background and objectives ................................................................................................................................. 4
   1.2. Organisation of this report ..................................................................................................................................... 5
2. METHODOLOGY ............................................................................................................................................................. 5
3. RESULTS AND DISCUSSION ........................................................................................................................................ 5
   3.1. ESTOC site ............................................................................................................................................................. 5
   3.2. PAP site ................................................................................................................................................................. 6
   3.3. Western Atlantic routes .......................................................................................................................................... 7
4. CONCLUSIONS AND OUTLOOK ............................................................................................................................... 8
5. REFERENCES ................................................................................................................................................................. 8
6. ACRONYMS .................................................................................................................................................................... 9
EXECUTIVE SUMMARY

Inter-comparisons of oceanic values obtained from different platforms and by different sensors or instruments, are essential to achieve a basin-wide and global consistency of observations. Inter-comparisons of instruments and sensors deployed under strict conditions, for a limited amount of time, are useful and provide significant insights, as those performed as part of FixO3 WP12. During long-term deployments, however cross-calibrations of systems installed on different types of platforms (buoys, moorings, ships), provide calibrations during the time of deployment.

Here we assess the cross-calibrations between the FixO3 time-series stations and ships in the eastern North Atlantic at the ESTOC and PAP sites, and between ships in the western Atlantic.

Results show that agreement is good between different types of sensors and instruments, and between different platforms, proving that such cross-calibrations are a valuable tool to maintain high standards in ocean observations.
1. INTRODUCTION

1.1. Background and objectives

New ocean pCO$_2$ sensors have arrived on the market in recent years, with different technologies that provide pCO$_2$ values using semi-permeable membranes, dyes, or spray-type equilibrator, that can be installed both on buoys and in research ships or commercial vessels, so called Volunteer Observing Ships (VOS). Most of the sensors designed for buoy deployments are initially calibrated by the manufacturer, but do not include any set of gas standards. All of them include a zero-CO$_2$ calibration option, assuming the calibration slope, over the concentration range being measured, keeps constant for long periods (which has proven to be not the case). Only the pCO$_2$ sensor by Battelle (Columbus, Ohio, USA) includes a span gas. However, its cost makes this sensor very specific, yet desirable, for long deployments. Any type of sensor should be inter-calibrated with other existing equipment that theoretically provides more accurate pCO$_2$ data. Inter-calibration exercises have been performed, deploying different types of sensors on the same buoy for long time periods of time. This has been part of FixO³ WP 12, providing valuable results. However, this exercise only provides information about the actual time the sensors were in the seawater and about the state of the art of the sensors used during the experiments. When a sensor is deployed on a buoy, it is important to have independent information to assess the accuracy of the values provided during the time of deployment.

In only some cases, buoys that are included in long-time series stations, are visited monthly (sometimes seasonal or even annually), when research groups can take samples for discrete measurements of two of the four carbonate system variables (pH, total alkalinity TA, total dissolved inorganic carbon DIC, and partial pressure of CO$_2$ (pCO$_2$)). When this happens, the measured pCO$_2$ or the computed values of pCO$_2$ (using pH and TA, or TA and DIC, or pH and DIC) can be used to follow any discrepancy between the sensor value and the discrete values, and can be considered for calibration purposes. However, we should keep in mind that computed values provide data with errors associated to both the input data sets and the best set of carbonate system constants selected.

Another important inter-calibration exercise takes place when the buoy providing pCO$_2$ data is located close to one VOS that includes a sea surface pCO$_2$ system (e.g. General Oceanics, Miami, USA), which has 4 different calibration gases traceable to the World Meteorological Organisation scale. The precision of these systems is greater than 0.5 µatm and the accuracy estimated with respect to the standard gases is of 1 µatm. When this happens, values provided by the buoy sensors can be improved. The only aspect that should be kept in mind is to consider any small temperature difference between the location of the sensor and the actual position of the ship line.

Our study has considered both types of inter-calibration possibilities in order to achieve the objectives of WP11.
1.2. Organisation of this report
In the Methodology section we describe the sites and instruments of the observations used. In the Results section, we show cross-calibrations in the eastern North Atlantic at the ESTOC and PAP sites, and show the potential for a new VOS line in the western Atlantic.

2. METHODOLOGY
For the inter-calibration exercise, data provided from time series stations which have discrete sampling, VOS line data, or sensor data have been considered. Two time series were selected: the European Time Series Station at the Canary Islands, ESTOC, located in the subtropical eastern Atlantic Ocean at 29º10’N 15º30’W, and the Porcupine Abyssal Plain (PAP) observatory in the North Atlantic at 49ºN 16º30’W. Both sites have been equipped with a pCO$_2$ membrane type sensor with zero gas calibration providing data with high resolution (several values per day). The ESTOC site has nowadays seasonal visits for discrete measurements and also has been visited for a VOS line with monthly resolution for pCO$_2$ from 2005 to 2012 which includes a General Oceanics system with four calibration gasses. VOS lines that cross the Atlantic pass close to the PAP site in the east and the new QUIMA VOS line (that joins New York (USA) with Montevideo (Uruguay); started in the last months) in the west.

3. RESULTS AND DISCUSSION
3.1. ESTOC site
Figure 1 depicts ESTOC sea surface monthly fCO$_2$ observations from a shower-head type equilibrator system as well as pCO$_2$(calculated from pH and TA) (1995 to 2004) and pCO$_2$ (calculated from TA and DIC) (2005 to the present) (Santana-Casiano et al., 2007, Gonzalez-Davila et al., 2010, Bates et al., 2014), together with the harmonic fit for the experimental data and the linear trend (purple line). VOS data were also included (black dots in Figure 1). The inclusion of those data does alter neither the harmonic nor the linear trend. Only two data from the VOS line where measured when the site was visited for discrete analysis to calculate pCO$_2$ from DIC and DIC. In this case the difference between data was ± 2.3 µatm that become ± 1.3 µatm when temperature in the VOS line location was corrected to that at ESTOC site. This low error includes both measured and computed errors but clearly confirm the accuracy of both systems. Starting as part of FIXO$^3$, PLOCAN has included a membrane type sensor in the ESTOC site that began to provide two observations a day (noon and midnight) from March 2015 (blue dots, Figure 1).

Figure 1: Monthly sea surface fCO$_2$ values at the ESTOC site over time, cross-calibrated: by an equilibrator system and discrete samples (purple dots), by VOS line (black dots), by buoy data (blue dots). The continuous purple line is the harmonic fit.
During 2015, the ESTOC site has been visited 4 times giving calculated pCO$_2$ from TA and DIC data that presented a difference of ± 3.7 µatm that became ± 3.1 µatm when temperatures were adjusted. The values did not present any trend that could be associated to any fouling interference (the pCO$_2$ sensor includes a seawater pump that inject seawater from out of the buoy influence). These values that, as indicated above, included both errors due to the sensor and to computed values, are well inside the accuracy expected from this inter-comparison. A more long term set of data should be considered in the future in order to follow the sensor response.

### 3.2. PAP site

Figure 2 shows a map of the north-eastern North Atlantic showing the location of the PAP station and VOS tracks; sea surface parameters show high variability in this region, caused predominately by the bathymetry of the region.

![Map of the north-eastern Atlantic around the PAP site. Showing Ireland as the gray patch, the bathymetry along the VOS ship tracks in colour, and the location of the PAP site as a large black dot at 49° N / 16° 30' W.](image)

Figure 3 shows the monthly mean sea surface pCO$_2$ measurements of the VOS lines (blue) and PAP site (red) over time from 2010 to 2015.

![Monthly mean sea surface pCO$_2$ data from the VOS line (blue) and the PAP station (red) from 2010 to 2015.](image)
Figure 4: Scatter plot of monthly sea surface $pCO_2$ from the PAP station versus monthly sea surface $pCO_2$ from the VOS line

Figure 4 shows the correlation of the monthly sea surface $pCO_2$ values from the PAP site with the monthly sea surface $pCO_2$ values from the VOS line; the $R^2 = 0.12$. Sea surface $pCO_2$ measurements at the PAP site show high variability, with a seasonal amplitude of up to 200 µatm, with the variability of any one month reaching 100 µatm (e.g. after October 2014, variability reached 100 µatm within a month). This is related to both biological productivity before July in the area and the seasonal heating cycle together with vertical mixing in the area (Hartman et al., 2010; Frigstad et al., 2015). Additionally, this explains the low correlation with the VOS measurements.

3.3. Western Atlantic routes

In the western Atlantic (Figure 5), with the inclusion of the new QUIMA VOS line crossing North to South West Atlantic will provide an important opportunity to improve the quality of the individual VOS line data obtained from three different VOS line: the UK-Caribbean line (UNEXE), the North Europe-North America (GEOMAR) and the aforementioned QUIMA line (UPGC). As is observed in Figure 6, the area is a highly variable region with important oceanographic features that strongly affect the sea surface temperature (Figure 6a), sea surface salinity (Figure 6b) and, consequently, the $pCO_2$ values of the surface waters (Figure 6c). Due to this high variability, it is very important to continue with this VOS development in order to try to get data that are coincident in both time and space among the three VOS lines.
Figure 6: Map showing parameters along the new QUIMA line in the western Atlantic, left the sea surface temperature (SST), middle the sea surface salinity (SSS), and right the sea surface fCO2.

4. CONCLUSIONS AND OUTLOOK

In this study we assess the cross-calibrations between the FixO3 time-series stations and ships in the eastern North Atlantic at the ESTOC and PAP sites, and between ships in the western Atlantic. The main conclusions from the study can be summarised in the following two points:

1. It is difficult to carry out inter-comparisons for buoy data with discrete analyses, due to errors associated with the determination of carbonate system variables and set of constants used. However, ESTOC data shows an important example of high accuracy among data determined with different methodological strategies.

2. Volunteer observing ships do not exactly follow the same tracks due to weather and sea-state, and increasingly change trading lines due to market forces; this makes it increasingly difficult to obtain continuous observations along the same line for long periods of time, causes difficulties in the inter-comparison exercises between VOS lines and buoys data, and among VOS lines themselves. However, when these factors do not occur, and when we can obtain data that are coincident in time (also in space), VOS data is an important tool for inter-comparison purposes and in order to provide high accuracy surface data.

Future work:

- Detailed, rigorous statistical analysis of cross-calibrations, e.g. at the PAP site.
- Continuous cross-calibrations as further measurements become available at ESTOC and PAP.
- Cross-calibrations between further stations and lines.
- Cross-calibrations between platforms newly added to the Surface Ocean CO2 Atlas version 4 (Bakker et al., 2016), to be released in September 2016.

5. REFERENCES


6. ACRONYMS

DIC total dissolved inorganic carbon
ESTOC European Time Series Station at the Canary Islands
fCO2 fugacity of CO2
FixO3 Fixed point Open Ocean Observatories Network
PAP Porcupine Abyssal Plain observatory
pCO2 partial pressure of CO2
SOCAT Surface Ocean CO2 Atlas
SSS sea surface salinity
SST sea surface temperature
TA Total Alkalinity
VOS Voluntary Observing Ships