Long-term intercomparison of two pCO_2 instruments based on ship-of-opportunity measurements in a dynamic shelf sea environment

Vlad A. Macovei[1], Yoana G. Voynova[1], Meike Becker[2], Jack Triest[3], Wilhelm Petersen[1]
[1]Institute of Coastal Ocean Dynamics, Helmholtz-Zentrum Hereon, Geesthacht, Germany
[2]Geophysical Institute, University of Bergen and Bjerknes Centre for Climate Research, Bergen, Norway
[3]4H-Jena Engineering GmbH, Kiel, Germany

Helmholtz-Zentrum hereon

Key Points

- We validated a membrane-based pCO_2 sensor against a traditional showerhead equilibrator style sensor
- The measurements between the two instruments were strongly correlated at crossover locations
- The higher observational resolution given by the membrane sensor allows identifying short-lived, biogeochemically-driven events
- As a corollary, the validation of the other FerryBox routes improves our observational coverage in the South and Central North Sea

Introduction and motivation

The contribution of the coastal ocean to atmospheric carbon dioxide uptake is difficult to estimate due to the heterogeneity of coastal seawater partial pressure of carbon dioxide (pCO_2) and the limited number of observations available. Ships-of-Opportunity equipped with instruments measuring the carbonate system parameters (SOOP-CO_2) have been used to increase our observational coverage. Showerhead equilibrator-style (SHS) instruments remain the 'gold standard' due to their small measurement uncertainty. More recently, membrane-based sensors (MBS) that require less frequent and less costly maintenance have been developed to simplify the measuring process.

In this study, we perform a crossover investigation between pCO2 measurements taken by a MBS integrated with a FerryBox and a conventional SHS on two long-term data sets in a dynamic coastal environment. The FerryBox dataset features a higher temporal and spatial resolution in the study area and these advantages are explored. By validating this new data set, we are increasing our observational capacity, in line with operational oceanography recommendations.

Methods and study area

The MBS and SHS instruments used in this study are a HydroC-FT (4H-Jena Engineering; uncertainty of ±1%) installed on the C/V *Lysbris Seaways* and GO-8050 (General Oceanics; uncertainty of ±2 µatm) installed on the M/V *Nuka Arctica* respectively. SHS data are available in the Surface Ocean Carbon Atlas database (www.socat.info) and MBS data are available in the FerryBox database (www.ferrydata.hzg.de). Seawater temperature was also measured on both ships.

The ship routes often overlapped in the Skagerrak Strait (Figure 1a). We selected valid crossovers when the two ships passed within 24 h of each other through five small sub-regions (Figure 1b). These regions are smaller than 32 km and typical daily water mass drift in this region is lower than that (www.coastmap.org). Furthermore, we removed potential crossovers where the variability of the pCO_2 or temperature results was too high during the passage through a sub-region.

We found no time difference or seasonal bias in the comparison. The difference in water temperature measurement location meant that *Lysbris* temperatures were often higher, but we found that a correction based on the temperature dependence of pCO_2 did not improve the comparison.

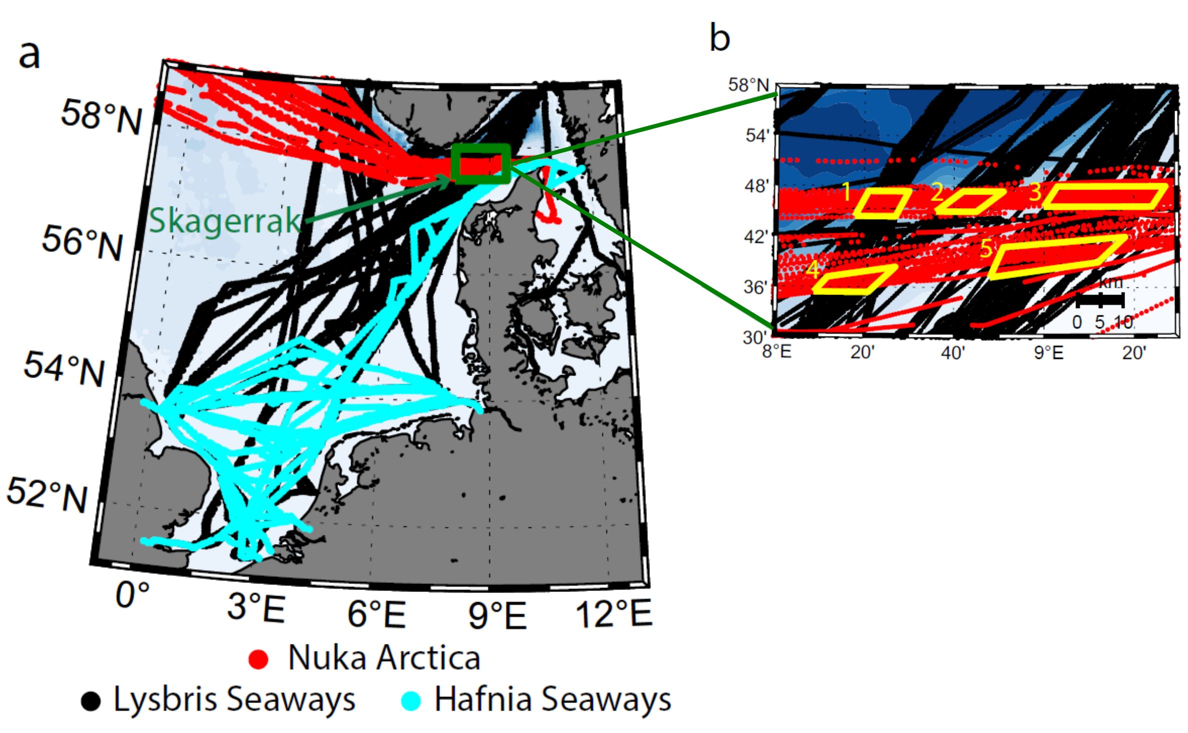

Figure 1: (a) Map of the south and central North Sea showing the tracks of the *Nuka Arctica* (red), *Lysbris Seaways* (black) and *Hafnia Seaways* (cyan) between 2013 and 2018. The location of the Skagerrak Strait is shown with the green box. (b) Zoom-in on the Skagerrak that identifies five sub-regions with the highest probability of valid crossovers between *Nuka* and *Lysbris*.

Crossovers in Skagerrak

During the five study years, 14 valid crossovers were identified with a mean difference (MBS - SHS) of 1.5 ± 10.6 µatm and a range between -16.9 and 25.0 µatm (Figure 1b). This is similar to other intercomparison experiments in the literature in spite of this study being done on two different ships, over a long period and in a dynamic coastal environment.

The MBS-equipped ship sailed through the Skagerak more often, which allowed identifying short-lived biogeochemical events such as the high pCO_2 values in autumn 2016 (highlighted in Figure 2).

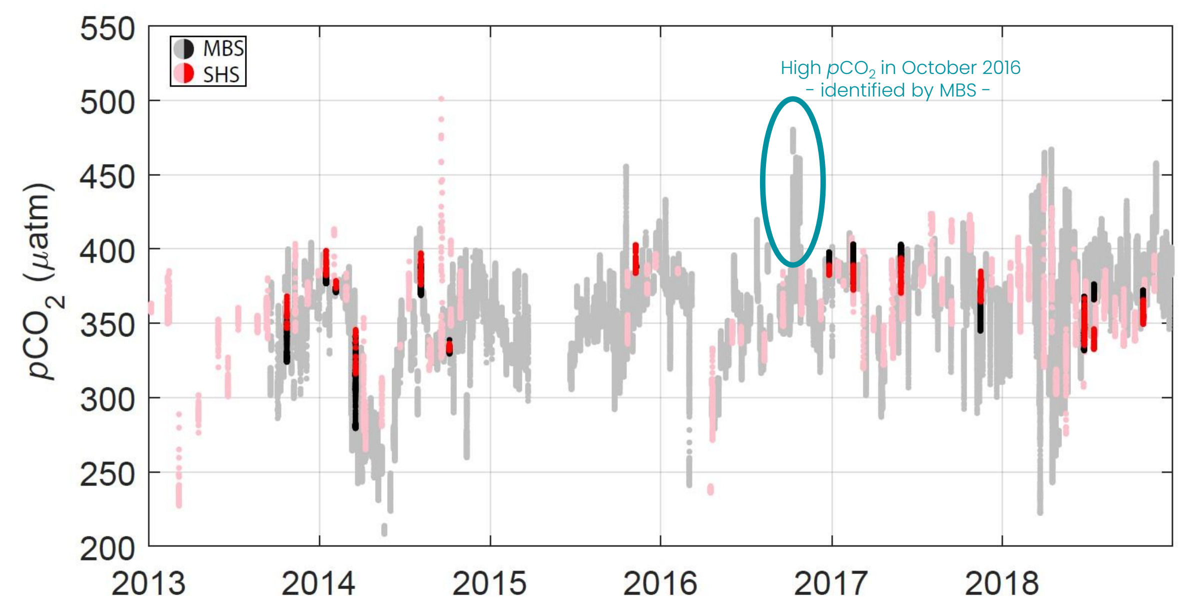

Figure 2: Time series of the pCO_2 measurements taken by the two different types of sensors (MBS on *Lysbris Seaways* and SHS on *Nuka Arctica*) in the restricted box in the Skagerrak shown in the zoom-in of Figure 1 (lighter shades) and an emphasis on the valid crossovers identified (darker shades). The horizontal axis tick labels represent the start of the respective year.

Implications for North Sea coverage

MBS-equipped FerryBoxes exist on other SOOP-CO_2 in the North Sea, such as the C/V *Hafnia Seaways*. *Hafnia* pCO_2 measurements can now be validated against *Lysbris* measurements by organising into 0.1° × 0.1° × 1 day bins (Figure 3b). We found a linear relationship with a slope of 1.06(±0.04) and a root mean square error of 22 µatm. The combined surface seawater pCO_2 datasets expand the FerryBox coverage to include the biogeochemically-significant dynamic areas in the southern North Sea and German Bight.

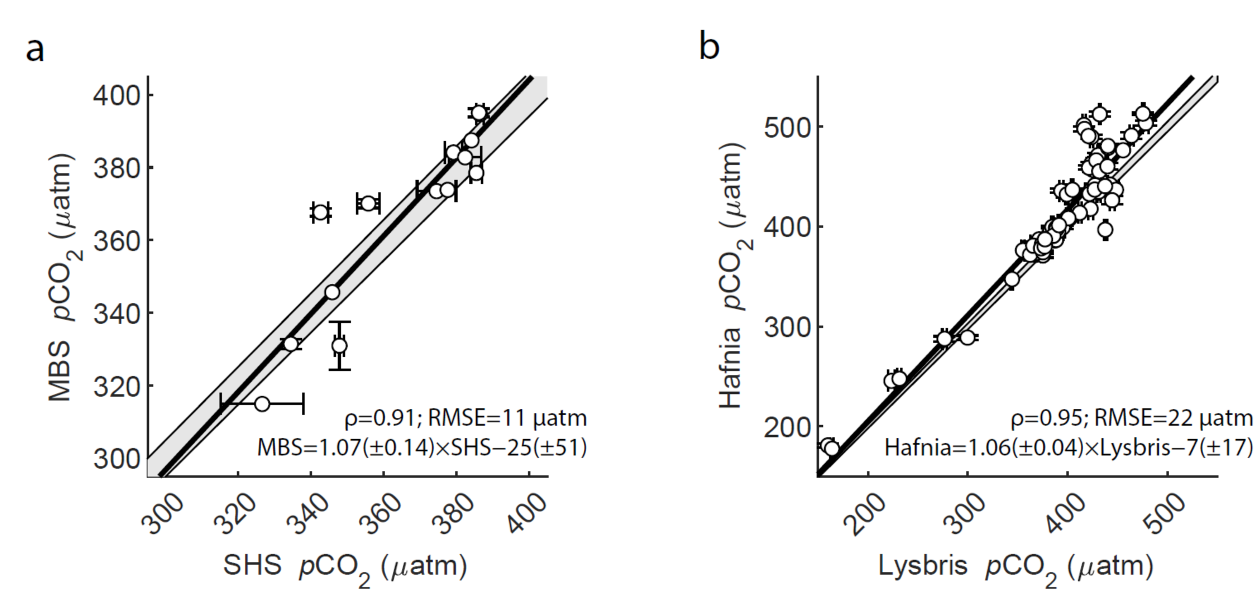

Figure 3: (a) Relationship between the seawater pCO_2 measured by the SHS on *Nuka* and the MBS on *Lysbris* at the valid crossovers identified in the Skagerrak. (b) Relationship between the seawater pCO_2 measured by two MBS on board FerryBox ships at valid crossovers across the North Sea. The subfigures include a 1:1 band (grey) rather than a line to include the intrinsic sensor uncertainties, a thick black line corresponding to the equation displayed and ± 1 standard deviation error bars for the averaging done at a chosen crossover location.

Publication available at: Macovei, V. A., Voynova, Y. G., Becker, M., Triest, J., & Petersen, W. (2021). Long-term intercomparison of two pCO2 instruments based on ship-of-opportunity measurements in a dynamic shelf sea environment. *Limnology and Oceanography: Methods*, 19(1), 37-50. doi:10.1002/lom3.10403

FerryBox · Universitas Bergensis · BJERKNES CENTRE for Climate Research · 4H JENA ENGINEERING

Helmholtz-Zentrum **Hereon** • Max-Planck-Straße 1 • 21502 Geesthacht I Germany • T +49 4152 87-0 • contact@hereon.de • www.hereon.de
Dr. Vlad Macovei, Dept. of Coastal Productivity • T +49 4152 87-2369 • vlad.macovei@hereon.de • Twitter @OceanVlad @FerryBox_Hereon