Review of doctoral dissertation "Characteristics of the marine CO_2 system in Arctic waters" submitted by Fernando Aguado Gonzalo

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Recommendation

The thesis takes a broad-based approach to the CO_2 system with papers focusing on biogeochemistry, thermodynamics and instrument development respectively. The CRediT author contribution statements in the three papers confirm that the candidate has shown the ability to conduct independent scientific work, taking a major role in all three papers: designing the studies; carrying out the research and analysis; writing the original drafts. I consider that the thesis constitutes a significant scientific contribution and recommend that it proceeds to an oral defence.

The thesis summary and the three papers are reviewed below in sequence.

Thesis summary

The summary begins with a clearly presented overview of the CO_2 system in seawater including the role of the ocean in taking up a significant proportion of the CO_2 released by burning of fossil fuels, and the resulting process of Ocean Acidification. The author makes a strong case for studying the CO_2 system in the Arctic Ocean which is undergoing rapid change as rising temperatures lead to larger ice-free areas and an increase in the already large freshwater runoff. The summary shows a clear grasp of the chemistry of the CO_2 system in seawater, and presents the aims formulated for each of the three papers. The summary also gives details of the state of the art methods used for the various measurements. Certified reference materials were used to ensure the accuracy of the TA, DIC and pH measurements.

Paper 1

This paper addresses the spatial and temporal variability of the CO_2 system in the surface waters of the Fram Strait over the years 2019-2021. The data analysis involves a wide-ranging discussion combining chemistry, biogeochemistry and physical oceanography.

The analysis of TA and DIC data takes as a baseline mixing between two endmembers, surface winter water and sea ice. This allows the measured values of TA and DIC to be compared with the theoretical mixing line. While primary production and respiration cause opposing changes in TA and DIC, calcification and the reverse process of carbonate dissolution cause changes in the same direction. Using the known ratios of TA and DIC changes for these processes, the paper has been able to show differing behaviour between the years studied. The year 2019 appeared to be dominated by photosynthesis, with a clear indication that the undersaturation in pCO_2 resulted in a significant net uptake to the ocean. In subsequent years the TA increase becomes less, and comparison with the changes in DIC indicates both a lower primary productivity and a shift towards calcifying organisms. These changes are ascribed to a shift towards lower temperature and proximity to the ice edge.

Three factors are considered to contribute to variations in pH in the study area: the largest being biological activity, followed by temperature and salinity changes.

Variations in pCO_2, the parameter that directly determines the study area's role as a sink for atmospheric carbon, shows small scale changes overlaid on a general dependence on primary production and temperature. Upwelling of nutrient-rich water, sea ice extent, and the movement of different water masses are discussed as additional factors affecting primary productivity and thus surface water pCO_2. Unravelling the relationship between these changes and their relative effects on surface pCO_2 will be an important focus for future studies, building on the insights generated in this paper.

Paper 2

This paper addresses the internal consistency of measured CO_2 system parameters in Arctic waters. This is an important contribution since Arctic waters differ from low- and midlatitude waters due to their low temperature, proximity to sea ice, and major freshwater inputs. The paper explores the extent to which two measured CO_2 system parameters can be used to calculate the rest of the CO_2 system while remaining within the accuracy limits established for weather-quality measurements.

All four CO_2 system parameters were measured at a number of open ocean and coastal stations. This allowed direct comparison between measured values and values calculated from two other CO_2 system parameters. The results, shown in Figures 2 to 5, are striking both in terms of the differences between oceanic and coastal waters and in the performance of different parameter combinations. The temperature difference between pH and pCO_2 measurements does not appear to have a significant effect on the results.

Although good performance was found for some parameter combinations in oceanic waters, the difference between calculated and measured DIC and TA was up to 2 times larger than expected from the uncertainties in the measurements and the constants. The authors suggest that the explanation may lie in the presence of organic alkalinity, which is consistent with the offset in TA in the oceanic waters in the upper two panels of Figure 2. It is, however, important to bear in mind that the CO_2 constants used, which were measured in Pacific waters, may not be fully applicable in this system.

The authors found a good linear correlation between TA and salinity. Using TA calculated from salinity instead of measured TA resulted some loss of accuracy in calculating CO_2 system parameters but the effect was generally small. This is a significant result since it opens the way to characterising the CO_2 system with a single measurement in these challenging Arctic conditions. This result could have been given greater prominence by extending Table 4 to include calculated TA as an additional input parameter.

The causes of the very different results in oceanic and coastal waters are beyond the scope of this paper. However, it is interesting to note that TA-salinity relationship has a large intercept (782 mol kg^{-1}) that is somewhat more than a third of the oceanic value. This indicates that the freshwater endmember is not just pure water but a solution with its own complex chemical composition where the assumption of standard seawater composition, which lies behind the CO_2 system constants, will not apply. Varying chemical composition close to the close may be part of the reason for poorer internal consistency in coastal waters.

The authors have used the CO_2 constants derived by Lueker et al. (2000) for their analysis, since these constants have been found to be the most relevant in other systems. The authors are to be commended for testing these constants against competing sets of constants available in CO2SYS. The results shown in Appendix C confirm the original choice of constants.

The results presented in this paper provide an invaluable guide for CO_2 system measurement strategies in the Arctic waters with a focus on ensuring compliance with weather-quality criteria.

<u>Paper 3</u>

This paper describes and tests a system for essentially simultaneous sampling for all four parameters of the CO_2 system together with salinity, temperature and depth from a standard CTD unit. An in-situ pump is attached to the CTD frame with an inlet close to the CTD unit. The approach is based on a system designed for trace metal sampling, and has been adapted to address the different sampling regimes for the CO_2 system parameters.

The first test was carried out in the Greenland Sea, where calculated pCO_2 was compared with pCO_2 calculated from simultaneous measurements of pH and total alkalinity. Although covering just 6 samples at different depths the agreement was excellent (0.9 ± 4.5 µatm). Despite the small sample size, it is interesting to note that larger scale comparisons using traditional Niskin bottle sampling reported somewhat larger uncertainties (± 5.0 and ±5.3 µatm). This suggests that simultaneous sampling can give superior results even though pCO_2 changed little over the upper 40m of the water column.

This highlights an important limitation of traditional Niskin bottle sampling. The CTD unit that measures salinity, temperature and depth is placed close to the bottom of the frame and below the Niskin bottles used for water sampling. Even if the water in the Niskin bottles is fully representative of the water over the bottles' depth range, the sampled water will represent an average of the water composition in the depth range ca. 0.1 to 1.1 m above the CTD unit. This difference may not be significant where the variations in salinity, temperature and target chemical species with depth are relatively small. However, in the presence of sharp gradients there will be a clear mismatch between the water sampled by a Niskin bottle and the temperature and salinity recorded by the CTD unit.

The superior capabilities of the pump sampling system are clearly illustrated by the measurements in the Svalbard fjords and the Vistula River plume. Both these systems show sharp gradients in the CO_2 system parameters in the upper few metres of the water column, features that would be completely missed by traditional Niskin bottle sampling. The sampling at 6 hour intervals in the Vistula River plume also shows that the CO_2 system parameters show strong temporal variation that appears to be associated with changes in salinity. These measurements used a vertical resolution of 0.5 m, but the authors have suggested that even higher resolutions may be possible. The good simultaneity of the salinity and pCO_2 system measurements is shown by the linear correlations between TA and salinity in both systems.

A wider implication of these measurements concerns the use of "surface water" pCO_2 measurements to estimate air-sea fluxes. These typically make use of a continuous flow using an input from ca. 2.5 m depth, alternatively Niskin bottles placed just below the surface. There is a clear risk that the resulting values do not represent the pCO_2 values at the water surface, particularly in near-coastal systems subject to stratification in the upper water column.

The development of this sampling system is an important step forward: I hope that it will continue to be used and also taken up by other marine institutes. It illustrates the importance of innovation in marine science: new sampling and measurement methods lead to new insights.

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