

Interactive comment on “Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies” by C. J. M. Hoppe et al.

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First a personal declaration. I reviewed the original submission of this work to BGD and recommended against publication largely because I felt that the experimental work was not presented (and perhaps not carried out) as well as the potential importance of the conclusion justified.

Since that time, I have had a number of discussions with the paper's primary author clarifying what I felt could be said with confidence, and what was more nebulous. The resulting paper is much modified, in part as a consequence of those discussions (see Acknowledgements).

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Now, to my review!

The subject of this paper is timely and important. It is central to laboratory and oceanic studies of ocean acidification that the CO₂ composition of the seawaters that are involved in such experiments be well characterized, and the uncertainty of parameters such as the p(CO₂) or the carbonate ion concentration be known. Insofar as these parameters are often difficult to measure directly and are often inferred from other measurements, there can be unacknowledged contributions to this uncertainty that if not recognized and dealt with will further complicate the understanding of such experiments.

This paper clearly points out that all is not well. In addition to their own measurements, they use a limited quantity of other published data to show that discrepancies in the predicted p(CO₂) value can be large, thus throwing doubt on other derived parameters such as carbonate ion concentrations. Unfortunately, neither the authors nor myself understand the source of these observed discrepancies. They are thus put forward to the community as a warning of what is currently being found (it could be worse in cases where such discrepancies are not even looked for).

I think that – as a result – it is a paper that is of value to the OA community as a caution even though it offers no solutions. It may (I hope) provoke the careful work that will be needed to resolve whether or not there is an underlying problem in our understanding of marine CO₂ chemistry, or whether the larger problem is in the methods we use to characterize the marine CO₂ system.

I thus feel it should be published, though – of course – I still have further comments that I hope the authors will address:

(1) I think they should make more strongly the case that OA researchers should, in any published work, be prepared to provide and defend an estimate of the uncertainty associated with their reported measurements of the various CO₂ parameters.

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(2) I disagree that agreeing on two parameters (pH & AT) will allow progress. First, it is probably best to measure pH and CT as then any errors in estimating $p(\text{CO}_2)$ or carbonate ion concentration will be independent of the additional uncertainties associated with all the possible non- CO_2 acid-base systems in the seawater. More importantly, unless the pH and CT measurements are of known uncertainty (i.e., a good QA/QC program is in place in the lab making the measurements), then it will still be difficult to have confidence that OA measurements in two different labs can sensibly be compared.

Interactive comment on Biogeosciences Discuss., 9, 1781, 2012.

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