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Biogeosciences Discussions

Interactive comment on "Potential impact of DOC accumulation on fCO_2 and carbonate ion computations in ocean acidification experiments" *by* W. Koeve et al.

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Comments on "Potential impact of DOC accumulation on fCO2 and carbonate ion computations in ocean acidification experiments"

SUMMARY: This paper looks at a great topic, presents previously published results in a newer way, and needs a lot of editorial work. A more thorough and traditional review is below.

GENERAL COMMENTS: I read this paper with great enthusiasm, as I have been thinking about the same issues in my own work. I have seen the same trends of disagreement in fCO2 calculated from TA and pH as from DIC and pH. As the field of research

into the oceanic carbonate system expands, this issue will become more and more important as researchers try to constrain acidification and CO2 flux estimates.

While a significant portion of this paper relies on previously published results (Kim and Lee, GRL 2009, "Significant contribution of dissolved organic matter to seawater alkalinity"), the authors do not attempt to conceal this fact, and instead use the presented work to recast their results with regard to acidification experiments. Specifically, the Kim and Lee 2009 paper discussed the experimental contribution of DOM to total alkalinity, while the presented work takes the same results and goes one step further to discuss the effect of DOM-based alkalinity on fCO2 estimates. In that respect the experimental results are not new, but rather an extension of previous work. Additionally, the presented work also spends considerable time comparing two sets of simple carbonate system calculations, one which includes a DOM contribution to alkalinity, and one which does not. Perhaps unsurprisingly, the estimates of fCO2 including DOM diverge significantly from those which do not. It is instructive, however, to see how this affects fCO2 estimates from different carbonate system parameter pairings, i.e. TA-DIC, TA-pH, DIC-pH.

The authors are appropriately careful to limit the scope of their conclusions to culture and (presumably small-scale laboratory or mesocosm) ocean acidification experiments. It is unfortunate that they could not expand their findings to in-situ data, since the culture experiments do not reflect real oceanic conditions (the initial nutrient concentrations in these experiments are extremely high, for instance). However, this work presents a starting point and several interesting ideas which can potentially improve oceanic carbonate research in the future.

All that being said, this manuscript needs a large amount of work, and shows a severe lack of editing and proofreading. I have undertaken to list as many editorial suggestions as I could below, first by broader points, then specific grammatical or syntax errors.

TECHNICAL COMMENTS:

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Methods:

The authors specify that TA analyses were performed on filtered samples, while DIC and pH analyses were conducted on whole-water samples. However, this presents a serious problem: how might particulate matter removed from the TA analyses contribute to alkalinity? This seems to be a poorly understood topic, but there must be charge sites on particulate matter which can bond with [H+] ions and thus contribute to alkalinity. If anything, the presented results may be conservative; that is, if particulates do indeed contribute to total alkalinity, then the carbonate alkalinity is overestimated even more than presented. At the very least, this deserves some mention in the Methods or Results section.

Additionally, the authors need to more fully discuss their total alkalinity measurement method. They cite the Kim and Lee (2009) paper, but that paper does not sufficiently describe the TA method either. In particular, the authors need to specify what type of titration was performed: end-point or Gran (incremental)? End-point titrations in complex solutions are highly problematic, while Gran titrations are considered much more reliable.

Results:

It would be helpful to explicitly state the a positive ΔfCO2 indicates that fCO2(CT-pH) is higher than fCO2(TA-pH). The notation of ΔfCO2 is a little confusing in that respect: a positive ΔfCO2 means that the 'real' fCO2 is actually lower than the fCO2(TA-pH).

More description of the modifications to the CO2SYS program is needed. Does the modified version simply count DOC as alkalinity and add it to TA? These calculations form the basis for a substantial part of this work, and need to be more transparent.

Nutrients and DOC both contribute to TA. Nitrate and phosphate are consumed as DOC is produced, but it is not apparent how nutrient consumption is offset by DOC production. In order for DOC production to really contribute to TA, it would have to

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more than offset the nutrient depletion. This is discussed in some detail in Kim and Lee (2009), but is worth summarizing here.

Equations detailing the carbonate system, especially Eqs. 5 and 6, need to be presented much earlier in the manuscript, probably in the Introduction. These equations are essential to understanding how the authors quantify TA, which forms the basis for the whole paper.

GRAMMAR AND SYNTAX (this is not a comprehensive list, just what I noted as I read)

P3798 L6, remove 'there' P3799 L16, rewrite "requires to perform. . ." P3798 L21-22, "Alternative explanations. . ." this exploration only takes up a couple lines of this manuscript, does not offer any quantitative results, and should not be mentioned in the Abstract as it is an almost insignificant part of this paper. P3799 L19, "have significantly developed through the recent two decades" improper syntax P3799 L24 (and throughout manuscript), "measurements where available" the correct word to use in this situation is 'were', not 'where' P3800 L1, remove "in a discussion paper" P3800 L6, "where" should be "were" P3800 L18-20, Confusing sentence. P3802 L18, DOM is a term which has not been previously defined in this paper. In addition, DOM and DOC are used frequently throughout the paper, but their relationship is not discussed. Can you use them to mean the same thing? P3803 L13, Δ[CO32-] decreases in Fig.2. P3804 L15, "CO2SYS-DOC code version". This is confusing. The authors need to come up with a notation for the modified version of CO2SYS, even something as simple as CO2SYSDOC. The first three paragraphs of the "A Model Experiment" section could use a rewrite, they are pretty hard to follow. P3805 L6, Change "behaviour" to "behavior" P3805 L7, Change to "specifically" P3805 L18, remove "Obviously", rewrite to "When CT and pH are used as input variables (Eq. 1). . ." P3806 L7 and throughout, "eclipses" should be "ellipses" P3806 L18, "requires to first" change to "first requires an estimate of the hydrogen. . ." P3807 L4, change to "total borate, fluoride, and sulfate" P3807 L18, change "a wrong pH" to "an inaccurate pH" P3808 L11, can you give a percentage of the "minor contribution" of the choice of constants?

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Interactive comment on Biogeosciences Discuss., 8, 3797, 2011.