Biogeosciences Discuss., 8, C905–C908, 2011 www.biogeosciences-discuss.net/8/C905/2011/ © Author(s) 2011. This work is distributed under the Creative Commons Attribute 3.0 License.



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

A. Dickson (Referee)

adickson@ucsd.edu

Received and published: 10 May 2011

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

Andrew G. Dickson

This is an interesting, though confusing manuscript (see other reviews). It builds on earlier observations (Hernández-Ayon et al., 2007; Kim & Lee, 2009) that phytoplankton in culture appear to exude (presumably organic) species that can be titrated with strong acid such that they contribute to measured alkalinity values; more accurately, the measured alkalinity exceeds that estimated from that calculated from pH and total

C905

dissolved inorganic carbon and assuming only inorganic species, and the difference grows as the phytoplankton population grows in batch culture.

These two papers note:

Our one final potential concern is that if the presence of such organic bases goes unrecognized, then the calculation of p(CO2) from another pair of carbonate systems parameters such as pH and AT or AT and CT is compromised and any CO2 flux estimates will be similarly in error. (Hernández-Ayon et al., 2007)

Another concern is that if the contribution of DOM remains unrecognized and is not taken into consideration, the prediction of surface pCO2 from pairs of carbon system parameters involving AT will be in error, and CO2 flux estimates across the air-sea interface will consequently be inaccurate. (Kim & Lee, 2009)

Dickson (2010) wrote:

Essentially any computation involving total alkalinity requires (as with borate) that the total concentrations and the various equilibrium constants of all these other acid base systems be known so that they can be accounted for (see Table 1.2). If they are not well known there will be an inherent uncertainty in the computed speciation. In the case of substantial organic contributions to the alkalinity such information may well not be available, and total alkalinity, though measurable, may not be fully interpretable.

This manuscript embellishes these comments: ignoring substantial organic contributions to the total alkalinity when using that alkalinity in calculations with other CO2 parameters to describe the solution speciation will necessarily result in errors. They then perform some simple calculations that illustrate the possible magnitude of such errors.

In fact, any person could do such calculations easily using readily available software such as CO2SYS or CO2Calc. Essentially, assume that the measured alkalinity will be too high by a specified amount (the assumed DOC-AT) and adjust the inorganic

alkalinity up accordingly before calculating. (Strictly this is only true if the organic bases contributing to DOC-AT are essentially unprotonated at the pH of the seawater, i.e. their acid dissociation pK values are more than one unit below the pH.)

Although I do have some significant comments and a number of minor ones (see below), this is essentially my main reservation. Given that the authors do not say anything that is new, but simply emphasize earlier concerns and place these in the context of ocean acidification experiments, is this a paper that should be published? My opinion is probably not, but then I feel I already understand this system quite well.

FURTHER COMMENTS ______ The first fault I see in the approach described here does not, I suspect, influence the results. The authors chose their archetypal organic base as one with a single acid dissociation constant with a value of 4.2 (at S = 35 and t = 25 °C). Insofar as its pK° at zero ionic strength at t = 25 °C is not defined, it could indeed be greater than 4.5, thus ensuring that it should be considered as a base in the expression for alkalinity (Dickson, 1981) however it is not clear that is necessarily the case.

In fact (as noted above), it is this low choice of pK that simplifies the calculations to a much greater degree than the authors chose to do so (they indicate they added an explicit term in CO2SYS for an organic acid of a specified pK – presumably always treating it as a positive contribution to alkalinity).

Furthermore, a pK of 4.2 does not seem to me to be appropriate to an easily imagined species. What is the functional group thought to be? How does this fit with the observation of Lee & Kim (2009) cited in lines 22-23 (p. 3803) that DOC-alkalinity increases almost in lock-step with DOC?

In the manuscript's discussion it is noted that there may be a number of ocean acidification experiments where this problem may have led to an error in estimating the p(CO2). The reader may be left with the impression that this is a problem with any system with significant DOC, however this is not necessarily the case. The key feature

C907

is recent significant phytoplankton growth, I suspect. Thus for many OA studies it may not be a big problem, though scientists should be aware of the potential for a problem (see e.g., comment by Gattuso).

Line 26 (p. 3804) – Please define your Δ values, e.g. "wrong – right".

Line 8 (p. 3805) – Should reference be to Dickson et al. (2007)?

p. 3806 – The symbol for free hydrogen ion concentration seems to change between line 6 and the equations. Also why is hydrogen ion the only chemical species that is written in italics? (Even on p. 3805)

p. 3807 – borate (line 4) ; ellipses (not eclipses) (line 14)

p. 3810 – "Gulf of California", not "California Bay", though similar phenomena were seen in San Diego Bay, and in San Quintin Bay (Hernández et al., 2007).

pp. 3810-3811 – It seems unlikely that there will be large accumulations of DOCalkalinity in coastal seas that are well flushed with open ocean waters. The suggestion that this may be so needs further justification than noting higher DOM levels.

Line 23 (p. 23) – I do not believe this is an explanation for the Hoppe et al. results. First their water, though from the North Sea, was analyzed prior to any laboratory growth of phytoplankton, yet the discrepancy they note is equivalent to that found for a DOC-alkalinity of 50 μ mol/kg (found only at the very end of the Lee & Kim experiments).

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