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Comment

## ***Interactive comment on “Potential impact of DOC accumulation on $f\text{CO}_2$ and carbonate ion computations in ocean acidification experiments” by W. Koeve et al.***

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Comment on “Potential impact of DOC accumulation on  $f\text{CO}_2$  and carbonate ion computations in ocean acidification experiments.”

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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

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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  $p(\text{CO}_2)$  from another pair of carbonate systems parameters such as pH and AT or AT and CT is compromised and any  $\text{CO}_2$  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  $p\text{CO}_2$  from pairs of carbon system parameters involving AT will be in error, and  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2\text{SYS}$  or  $\text{CO}_2\text{Calc}$ . Essentially, assume that the measured alkalinity will be too high by a specified amount (the assumed  $\text{DOC-AT}$ ) and adjust the inorganic

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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  $t = 25\text{ }^{\circ}\text{C}$ ). Insofar as its  $\text{pK}^{\circ}$  at zero ionic strength at  $t = 25\text{ }^{\circ}\text{C}$  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  $\text{p}(\text{CO}_2)$ . 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

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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).

Minor comments ——— Line 23 (p. 3804) – The decision to have a fixed DOC-alkalinity despite the large changes in  $p(\text{CO}_2)$  inherently means that the  $pK$  of the species needs to be less than about 6.

Line 26 (p. 3804) – Please define your  $\Delta$  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 DOC-alkalinity 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  $\mu\text{mol/kg}$  (found only at the very end of the Lee & Kim experiments).

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