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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 F Hofmann (Referee)

ahofmann@mbari.org

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In their BGD contribution "Potential impact of DOC accumulation on fCO$_2$ and carbonate ion computations in ocean acidification experiments" W. Koeve et al. provide evidence that dissolved organic matter (DOM), especially in concentrations higher than in situ in the open ocean such as in mesocosm studies or in coastal and estuarine systems, significantly contribute to the alkalinity of sea water samples, leading to errors in carbonate system parameter calculations that rely on total alkalinity (A_T) and total dissolved inorganic carbon (C_T) as well as standard chemical descriptions of seawater that do not explicitly include dissociation and association of weak organic acids in

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DOM. Their results are highly relevant and useful, both for the design and evaluation of laboratory and mesocosm experiments dealing with the effects of elevated CO_2 levels, as well as for global ocean modeling efforts. The findings of Koeve et al. are furthermore especially important for biogeochemical models (including acid-base chemistry and the speciation of the carbonate system) of coastal and estuarine ecosystems with often routinely high DOM contents.

Overall, this is a very interesting paper, which I read with great pleasure. Past work brought me in contact with modeling and implementation of the general chemical sea-water description (e.g. Hofmann et al., 2008, 2010b,a) and adding a provision to in-clude weak acids with various pK's in a modular fashion to address DOM acidity in calculations in the aquatic acid-base calculation package AquaEnv (Hofmann et al., 2010b) was already considered. The work presented here shows that the acid-base contribution of DOM should definitely be included in standard calculations of seawater properties. There is a definite need for further field- and mesocosm studies as well as laboratory experimental studies to identify dominant DOM acids and more accurately determine their pK values as functions of temperature, salinity and pressure to correctly implement the respective effects in standard software packages.

General Comments

- in no particular order -

- The effect of weak organic acids might be important for two things: for fCO_2 calculation (i.e. for acid-base equilibration/speciation calculations as described in this paper) but also for alkalinity (A_T) determination itself. If A_T values are obtained based on titration curve fitting procedures (Dickson, 1981; DOE, 1994; Anderson et al., 1999; Zeebe and Wolf-Gladrow, 2001; Dickson et al., 2007, e.g.)

that use the "standard" chemical model of seawater, then organic acids present a problem since they are not explicitly included in the chemical model underlying the curve-fitting procedures. If A_T values are obtained based on end-point titration with a fixed end point (e.g., backtitration Anderson et al., 1999), then the effect of organic acids is included in the value obtained. For on end-point titration using a dynamic end-point obtained by evaluations of (modified) Gran equations (e.g. Gran, 1952; Hansson and Jagner, 1973; Bradshaw and Brewer, 1988a; Haraldsson et al., 1997), organic acids might again pose a problem since they are not included in the model underlying the equations. If the A_T determination procedure is based on the purely graphical (or by mathematical polynomial fitting and inflection point determination by evaluating derivatives) identification of the two inflection points of seawater titration curves (e.g. Dyrssen and Sillen, 1967; Dickson, 1981; Skoog and West, 1982; Bradshaw and Brewer, 1988a), then, if the two inflection points are still clearly identifyable over the effects of the organic acids, the effects of the organic acids are included in the obtained values. This problem with the determination of A_T values should be mentioned in the current paper and the A_T determination method used here should be explicitly given.

- The authors should elaborate more on how exactly they define "DOC-alkalinity", how they obtain concentration values for it, and how exactly they include it in their calculations. Most likely they assume a theoretical, monoprotic, weak acid HA with [DOM] = [$\sum$ HA] with a pK of 4.2. Following the rule given in Dickson (1981), since this pK is below 4.5 (defined for 25 °C and zero ionic strength by the way), this would mean to add HA as a proton donor to the definition of total alkalinity, i.e.

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + ... - [HA]$$

Consequently this would mean that the given "DOC-alkalinity" is calculated by determining [HA] from [DOM] by assuming [DOM] = [$\sum$ HA] and using the ambient pH to calculate the degree of speciation and then subtracting "DOC-

alkalinity" (=[HA]) from the "common" A_T values. If [A$^-$] is assumed to be "DOC-alkalinity" and determined values are added to A_T values, this would not be in line with Dickson (1981) which would have to be justified (However, if consistently used, this non-Dickson-approach would also yield correct results). Anyway, all this is just guesswork on my part, the authors should explicitly state their approach/calculations.

- Furthermore, it should be discussed why exactly a pK of 4.2 is chosen (cf.: with a pK of > 4.5, adding "+[A$^-$]" to the definition of A_T would be in line with Dickson (1981)) and why it is justified to lump all acid-base characteristics of DOM into one single theoretical monoprotic acid. (Have calculations with let's say 2 different assumed acids been performed?)

- It is not necessary to distinguish between Eqs. (1) and (3), (3a). As the authors already state, plugging (3a) into (3) yields (1). Generally, [CO$_2$] is always calculated using Eq (1), only in the "C_T, pH" case, [H$^+$] calculated from pH directly feeds into the equation and in the "A_T, C_T" case [H$^+$] needs to be calculated from the definition equation of A_T (e.g. Eq. (5)) and the measured A_T value using (a variation of) the described iterative solution procedure. Since not necessary, removing Eqs (3) and (3a) would facilitate reading. However, in the case of Eq. (2) it might actually be beneficial to not give the reduced version that is given here, but to state that, also in this case, [CO$_2$] is calculated with Eq. (1), but

$$C_T = \frac{(A_T - A_{minor})\left([H^+]^2 + K_1[H^+] + K_1K_2\right)}{K_1[H^+] + 2K_1K_2}$$

While this equation is a little bit more complex, it might facilitate understanding because it explicitly features A_T, does not contain A_C which is not properly defined yet at this point in the paper, and explicitly shows how the equation is derived (i.e. via $A_C = (A_T - A_{minor}) = [HCO_3^-] + 2[CO3^{2-}] = \left(\frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} + 2\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right)C_T)$

- Both DOM and POM can contribute to acid-base chemistry, as the surface of OM particles can provide surfaces/chemical groups for proton adsorption/desorption. This fact should be mentioned and, despite the procedural difficulties involved with performing measurements in solutions containing particulates, more detailed experiments focusing on this point and treating samples accordingly (filtration vs. no filtration) should be part of future studies.

- The pH value needed to calculate $[H^+]$ is the free scale pH. The authors should mention on which pH scale they obtain their (measured) values and how exactly they convert, if applicable.

- The authors mention that they check for errors introduced by different choices of dissociation constants and state that those errors are "small". A few numbers should be given here, together with references for the dissociation constant descriptions used, maybe in the form of a table.

- The practise of using $fCO_{2(C_T, pH)}$ as a reference to calculate ΔfCO_2 is acceptable given the working hypothesis of this paper and the underlying data set, but true measurements should be used in the long run to solve this problem.

- As an addition, the authors might want to relate their work to older work done on the same (or at least a similar problem) by Bradshaw and Brewer (1988a,b), where inconsistencies between data obtained by potentiometric titration (with subsequent calculations based on the standard chemical model description of seawater) and gas extraction methods were found. Bradshaw and Brewer (1988a,b) describe a potentiometric titration procedure where A_T and C_T are obtained from the position of the two inflection points of seawater titration curves (e.g. Dyrssen and Sillen, 1967). In their results for open ocean data (with presumably low DOM levels), A_T determination seemed to work fine (i.e. the position of the second inflection point of the seawater titration curve was correct), but their

C_T values were about 20 μmol kg^{-1} higher than values obtained by gas extraction (i.e. the position of the first inflection point of the seawater titration curve seemed incorrect). Bradshaw and Brewer (1988a,b) ascribe their findings to the possible existence of an unknown monoprotic acid with a pk between 6 and 8.7 - thus considerably higher than the "DOM acid" postulated here. So, while this most likely describes another (unknown) acid, it might be worthwhile to relate it to the presented DOM work.

- The modified CO2SYS code the authors produced should be made publicly available, both to make the approach presented here more transparent and for other researchers to use to analyze their data. This is important, even if the code is not highly "polished" yet, as it provides a rapid way for other researchers to analyze their data using the presented approach until the acid-base effects of DOM are routinely included in common seawater property calculation programs.

Minor comments

everywhere: use consistent notations, axis labelings, and subscripting!

p. 3798, l. 06: the notation "Δ" is usually used for a difference, not a "percent change" quantity. ΔfCO$_2$ is thus not intuitive and rather confusing. Another notation would help to avoid confusions.

p. 3798, l. 16: Here and throughout the paper: use "dissolved organic matter" (DOM) instead of "dissolved organic carbon" (DOC), since the nomenclature DOC really just means the C atoms contained in DOM - so DOC does not contain any acids or bases, but DOM does. So, even if DOM is expressed in terms of moles of organic carbon per volume or mass, DOM should be used here, not DOC.

p. 3800, l. 09: "ΔX=" is missing before 4.6

p. 3802, l. 15: missing subscript for $(A_T + C_T)$

p. 3802, l. 16: and troughout the paper: if C_T and A_T are used in subscripts, also use capital T and subscript and don't use a "+" sign as both quantities are not added to each other, i.e., fCO$_{2(A_T, C_T)}$ instead of fCO$_{2(At+Ct)}$

p. 3803, l. 01: and throughout the paper: don't omit charges from molecule notations: NO$_3^-$ instead of NO$_3$

p. 3804, l. 11-20: rather convoluted and confusing sentences, please rewrite

p. 3804, l. 27: Assumingly, the"fCO$_2$(measured)" value here means the fCO$_2$ value calculated with the modified CO2SYS version. "(measured)" - which should be in subscript by the way - is confusing here. Please choose a clearer notation. - A table showing input variables and fCO$_2$ values calculated with the original CO2SYS version and the modified code (also here, better notation/naming please) could help to clarify things and introduce what has been done.

p. 3808, l. 19: 90% or 49%?

p. 3809, l. 08: "measured and computed A_T": please clarify: they measured A_T and you calculated A_T including your DOC-alkalinity? If you did the calculations, how exactly? If they measured and calculated, from which parameter (pairs), using which TA determination method (see above)?

p. 3809, l. 08: again, measured and computed, this time apparently both by Hernandez-Ayon et al.: please mention how exactly A_T has been calculated and measured.

p. 3809, l. 12: It seems like the references Hernandez-Ayon et al. (2007) and Camiro-Vargas et al. (2005) are both used to describe the same experiment. Is this correct?

Section 5: Most likely the paper would benefit if this section was split up in a section "implications for ocean acidification experiments and global biogeochemical modeling" followed by a true "Conclusions" section.

Figure 1: please use square brackets on the axis to indicate concentrations: e.g. $[NO_3^-]$ instead of NO_3^-

Figure 2: please use "2-" instead of "- -" to indicate a double negative charge

all Figures: please use consistent notation to indicate the units: either "/ unit" or "(unit)" - preferably the former.

Andreas F. Hofmann

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