

Interactive
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.

W. Koeve et al.

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General response:

First, we like to thank the three referees and authors of two additional comments for their suggestions. Before responding to comments, critics and suggestions in detail, we like to emphasize a few aspects.

The primary intention of this paper is to make the community of researchers working in the field of ocean acidification aware of a potential problem when $f\text{CO}_2$ is computed from the recommended measurements of A_T (alkalinity) and C_T (total CO_2) under certain experimental conditions. We give an example from a series of culture experiments

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where the accumulation of DOM correlates with a clear and significant error if $f\text{CO}_2$ is computed from the pair of A_T and C_T . By means of simple model computations we argue that organic acids known to contribute to observed DOM accumulations elsewhere could explain the magnitude of the observed computational error. The role of DOM-alkalinity contributing to total alkalinity had been proposed before from a number of estuarine and coastal studies. The recent paper by Hunt et al. (2011, BG) quantifies in addition how this translates into an overdetermination of pCO_2 in river waters.

It is of course difficult (or impossible) and clearly beyond the scope of our work to extrapolate from our few experiments to any other individual OA-experiment done in the past or in the future. Experimental conditions are certainly highly variable. It is, however, worrisome that $f\text{CO}_2$ as an often used master variable in OA research is in most cases computed instead of being measured. It is perhaps even more critical that until this study was drafted the number of overdeterminations of the CO_2 -system in such experiments was almost nil. Still in many publications the computed $f\text{CO}_2$ is given without any error estimate.

The work of Hoppe et al. (BGD-2010, BG-2012) which stimulated the first author of this work to take a look into the $f\text{CO}_2$ -error associated with the difference of measured and computed A_T of the published work of Kim and Lee (2009), together with the results of this work suggest that one should be very careful in assuming that computed $f\text{CO}_2$ from experimental work is free of random or systematic errors. To demonstrate this issue of uncertainty is the prime intention of our work.

Given that direct measurement of $f\text{CO}_2$ is often impractical in experimental studies (e.g. due to small available sample size), what might be the most pragmatic way to reduce this addressed $f\text{CO}_2$ -computation uncertainty? In fact, we do not suggest to solve the DOM-alkalinity issue for OA experiment by adding measurements of DOC, DOM-alkalinity and/or its pK -distribution, as this would be even more impractical and usually well out of the focus of the experimentalists. Instead we suggest to carry out more experiments where at critical times of the experiments the CO_2 -system is

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overdetermined, either by adding precise pH measurements or where possible direct measurements of $f\text{CO}_2$.

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Referee 1 (D. Hansell)

Comment: General Comments:

Koeve et al investigated the inconsistencies between measured and calculated $f\text{CO}_2$ as evidenced in manipulated phytoplankton culture experiments. Consistent with prior reports for the role of DOM in affecting the total alkalinity of a system, and thus variables calculated from TA, they found that the high DOM concentrations occurring during 'ocean acidification experiments' introduces significant error in calculations of carbon system variables. They point out that software tools such as CO2SYS do not account for the proton acceptors in DOM, so calculations of $f\text{CO}_2$ will be and are incorrect in high DOM systems. They warn that global ocean biogeochemical models need to address this problem in coastal zones, where DOM may be elevated enough to make a difference. Overall the paper is well thought out and presented. The science presented was cleverly done; the authors used existing data from a prior publication to make their case. The effort is a timely one given the high interest and use of mesocosm studies at present. **Answer:** We thank Prof. Hansell for the encouragement and kind words.

Comment: *Specific Comments: Another paper from which delta DOC/delta NO3 data can be retrieved for inclusion in Fig. 7 is that by Goldman et al., 1992 (MEPS).*

Answer: Data from this paper will be included.

Comment: *Where is 'California Bay'? I have not heard of this place. In looking at the reference, I see that the authors are referring to the 'Gulf of California', also known as the 'Sea of Cortez', but not known as 'California Bay'.* **Answer:** Corrected.

Comment: *The first paragraph of the 'Conclusions' is written as a summary instead.*

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A summary is not necessary for this short paper. Revise so that conclusions and recommendations alone are found in this section.

Answer: We agree and will rewrite accordingly.

Comment: *As an aside, from someone who is not expert in the science of DIC: Koeve et al used as their motivation the 'discussion paper' by Hoppe et al. 2010, a paper which apparently has not advanced to 'full publication and acceptance' by the journal. I wonder if, given the results of Koeve, Hoppe et al should be reevaluated. Hoppe's main finding was 'Calculated $p\text{CO}_2$ matched measured $p\text{CO}_2$ if pH and TA or pH and DIC were chosen as input parameters, whereas $p\text{CO}_2$ calculated from TA and DIC was considerably lower than measured values.' It appears from the work of Koeve et al that the Hoppe finding is what should be expected given the experimental setup (i.e., Hoppe mesocosms started with 111 $\mu\text{mol/L}$ of NO_3 , so high DOC would result). Hoppe et al may not have realized why the discrepancy existed, but they certainly observed it. The Hoppe et al reviewers did not trust the discrepancy reported. According to Dickson, 'there are too many ways in which the quality of the experiment is unclear, particularly given the potential significance were the reported observations to be correct.' Wanninkhof wrote that 'the magnitude of the deviation. . .rais(es) questions of experimental execution'. The reviewers have many valid criticisms that Hoppe et al should take to heart, but it may be that on the most fundamental level Hoppe et al reported a valid finding; and their execution, though perhaps imperfect, resulted in findings that are nonetheless meaningful and important. Having apparently been rationalized and validated by Koeve et al., should Hoppe et al now rise to the level required for 'acceptance' by the journal? This outcome could be considered by the editor given Dickson's statement, regarding Hoppe et al, of 'the potential significance were the reported observations to be correct.' The observations of Hoppe appear correct based on Koeve, so the Hoppe paper emerges as significant, right? If Hoppe's main finding is still problematic, then we might conclude that Koeve is problematic. But the reviewers have not yet identified a major problem with Koeve, so. . . round and round we go.*

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Answer: This issue is solved. A revised version of the Hoppe et al. paper has been published this month, July 2012.

Comment:

Technical Corrections:

Page 3799/Line 10: should be 'An obvious approach is..' **Done.**

3799/16: delete 'to perform' **Done.**

3800/8: 'were found' **Done.**

3800/17: 'Such software applies established models. . .' **Done.**

3800/26: 'and how neglect of DOC' **Done.**

3809/14: When starting a sentence with 'this', 'this' must be defined. 'This' what? The authors may mean 'This finding', but the reader should not be required to guess. **Done.**

3810/10: should be 'decrease'

3810/23: I dont know what is meant in the sentence starting with 'So far...' because the word 'comprising' is not used correctly. I cant guess what is intended, but it needs to be fixed. **Changed to 'comprehensive'.**

3811/20: 'from', not 'form' **Done.**

Remove commas: at end of 3800/15, final comma in 3810/28, first comma at 3811/15, at 3814/15. **Done.**

Answer: Thanks for careful checking of the manuscript!

Referee 2 (A.F. Hofmann)

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Comment: *In their BGD contribution "Potential impact of DOC accumulation on $f\text{CO}_2$ 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 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 seawater description (e.g. Hofmann et al., 2008, 2010b,a) and adding a provision to include 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 $f\text{CO}_2$ calculation (i.e. for acid-base equilibration/speciation calculations as described in this paper)

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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 an 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 identifiable 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.

Answer: Kim and Lee (2009) evaluated TA based on the non-linear curve-fitting of titration data (Dickson, 1981, DOE 1994). This method gives TA values arising from all dissolved species including DOM and other unknown inorganic species in seawater. When this method evaluates TA, it uses a chemical model which can estimate individual contributions of all known species to TA (for example, borate, phosphate, silicate, sulfate, fluoride alkalinity) using total concentrations of those individual species and the corresponding dissociation constants. However, the present chemical model does not explicitly include DOM because up until now we don't know its contribution to TA and its dissociation constants. The bottom line is that regardless of TA evaluation procedures (non-linear curve fitting, Gran function, and etc), TA calculated from titration data using

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various evaluation procedures somewhat include DOM alkalinity component, although the exact magnitude of DOM TA can not be estimated.

In the final manuscript, we provide a more detailed description of the alkalinity analysis, in particular the endpoint detection.

Comment: *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.*

$$AT = [HCO_3^-] + 2[CO_3^{2-}] + \dots - [HA]$$

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 AT 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.

Answer: We have rewritten section 3.2 (A model experiment) of the manuscript. In the new version we describe the modifications we made for our CO2SYS-DOM version in much more detail. We also discuss in more detail the results of Fig. 6 of the BGD manuscript which was only briefly mentioned in the BGD version of this paper. This figure explores the sensitivity of our results to the assumption of our standard pK_{Org} by exploring a wide range of values for pK_{Org} . The figure clarifies that for pK_{Org} values

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well below typical seawater pH (and given DOM-alkalinity) we get a basically constant ΔfCO_2 signal. To be in better agreement with Dickson (1981) we have further changed the default pK_{Org} in CO2SYS-DOM to a value > 4.5 . This modification did not affect the results of our computations in any significant way.

The H^+ donor (acceptor in the titration) we had in mind was the carboxyl-group for which pK -values around 4 (e.g. Cai et al., 1997, p474a) have been reported. A pK of 4 is also assumed in the study of Millero et al., 2002. Carboxylgroups are widely distributed in nature, in humics, aminoacids, glycolates etc. The later are often mentioned as products of phytoplankton excretion. In fact, as shown in Fig. 6, we find similar on ΔfCO_2 as long as the pK_{Org} is well below the typical pH of seawater.

Comment: *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?)*

Answer: As mentioned already the calculations shown in Fig. 6 indicate that the effect is not restricted to a pK value as low 4.2, the value we used in our original model. In fact we found no literature data which would allow to specify the pK_{Org} distribution of freshly exudated DOM. We agree with the reviewer that more research would be needed before the potential effect of DOC-alkalinity on the fCO_2 computation could be plugged into tools for the routinely computation of CO_2 -system properties. Given the diverse nature of DOM (in particular under experimental conditions) and also its reactivity (e.g. formation of TEP, uptake by bacteria) and hence change over time, we do not expect that there is a stable (predictable) pK_{Org} distribution to be expected. Consequently we do NOT suggest to add detailed DOM determinations as default measurement variables to OA experiments for the sake of correct computation of fCO_2 from A_T and C_T data.

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Comment: *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*

$$C_T = \frac{(A_T - A_{minor})([H^+]^2 + K_1[H^+] + K_1K_2)}{K_1[H^+] + 2K_1K_2} \quad (1)$$

While this equation is a little bit more complex, it might facilitate understanding because it explicitly features A_T , does not contain AC which is not properly defined yet at this point in the paper, and explicitly shows how the equation is derived, i.e. via

$$A_C = (A_T - A_{minor}) = [HCO_3^-] + 2[CO_3^{2-}] = \left(\frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} + 2 \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \right) C_T$$

Answer: Originally (BGD) our discussion was guided by the equations given in Dickson et al. 2007. In restructuring section 3.2 we followed the suggestion of the reviewer applying the first equation given above to illustrate the AT+pH case better.

Comment: *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.*

Answer: The role of phytoplankton and bacterial cells to measured alkalinity of seawater has explicitly been studied in another publication (Kim et al., 2006, L&O, 331-338). In that study alkalinity determinations from filtered and unfiltered subsamples have been compared. We agree that this can provide an additional source of uncertainty to the computation of pCO_2 in experimental work, which, however, was intentionally excluded from the experiments of this study. We will briefly mention this aspect in the discussion section.

Comment: *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.* **Answer:** pH was measured on the total scale. CO2SYS converts internally to the free pH scale. Both is mentioned in the final version of the manuscript.

Comment: *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.* **Answer:** This will be provided with the revised version of the manuscript.

Comment: *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.* **Answer:** We generally agree. However, it is important to note here that experimental designs and small amount of sample from culture or mesocosm experiments often do not permit the measurement of fCO_2 with accepted standard methods (equilibrator, IR detection, etc). Evaluation of available small volume measurement techniques for fCO_2 is beyond the scope of this paper. We hesitate to suggest measurements which we know are often impractical or have not been rigourously validated against standard techniques.

Comment: *As an addition, the authors might want to relate their work to older work*

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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 $20 \mu\text{mol kg}^{-1}$ 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. **Answer:** This has been discussed in some detail in Kim and Lee (2009) and will therefore not be repeated in this paper.

Comment: 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. **Answer:** The code of CO2SYS-DOM will be made available to the public through the GEOMAR publication repository and a link to this repository item will be included in the final version of the paper. The reviewers shall receive a copy of CO2SYS-DOM with the revised paper.

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Minor comments

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everywhere: use consistent notations, axis labelings, and subscripting! **Answer:** We will double-check the ms accordingly after all changes to text and figures have been done.

Comment: *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.*

Answer: We have introduced our usage of Δ terms in the introduction and follow procedures used in open ocean studies published elsewhere.

Comment: *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.* **Answer:** We agree. This has been corrected in text and figures accordingly. DOM will be used as the generic term, DOC will be used only when explicit measurements of DOC (in carbon units) are reported.

Comment:

p. 3800, l. 09: " $\Delta X =$ " is missing before 4.6 **Corrected.**

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

p. 3802, l. 16: and throughout 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 $fCO_{2(A_T + C_T)}$ **Corrected.**

p. 3803, l. 01: and throughout the paper: don't omit charges from molecule notations: NO_3^- instead of NO_3 **Corrected.**

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

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rewrite **Answer:** We have rewritten section 3.2 and the description of the model experiments has been improved in the final version of the manuscript.

Comment: p. 3804, l. 27: *Assumingly, the " $fCO_2(\text{measured})$ " 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.* **Answer:** In the final version of the ms we refer to $fCO_{2(\text{imposed})}$ for this aspect. Also we have restructured section 3.2 being more explicit about when computations are done with CO2SYS-DOM or the standard version of CO2SYS.

Comment: p. 3808, l. 19: 90% or 49%? **Answer:** The meaning is "About 90% (49%) ... used A_T (C_T), respectively, as one of the measured variables." We agree that the sentence was too long to read easily. It has been rewritten.

Comment: 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)?* **Answer:** This is clarified in the final version of the paper.

Comment: 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.* **Answer:** See last comment.

Comment: 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?* **Answer:** This is clarified in the final version of the manuscript.

Comment: *Section 5: Most likely the paper would benefit if this section was split up in*

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a section "implications for ocean acidification experiments and global biogeochemical modeling" followed by a true "Conclusions" section. **Answer:** This will be considered for the final version of the paper.

Comment: Figure 1: please use square brackets on the axis to indicate concentrations: e.g. $[\text{NO}_3^-]$ instead of NO_3^- **Answer:** Done.

Comment: Figure 2: please use "2-" instead of "- -" to indicate a double negative charge **Answer:** Done.

Comment: all Figures: please use consistent notation to indicate the units: either "unit" or "(unit)" - preferably the former. **Answer:** Agree, corrected.

Referee 3 (A. Dickson)

Comment:

This is an interesting, though confusing manuscript (see other reviews). It builds on earlier observations (Hernandez-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 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 CO_2 flux estimates will be similarly in error. (Hernandez-Ayon et al., 2007)

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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 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 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 CO_2SYS or CO_2Calc . 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.

Answer: The quoted statements of Hernandez-Ayon et al. (2007), Kim & Lee (2009)

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and the 'Best practice book' chapter by Andrew Dickson provide the reader with qualitative concerns ('our final potential concern', 'total alkalinity ... may not be fully interpretable'). But has this qualitative concern impacted on measurement strategies or provided an awareness of the problem of the uncertainty of the computation of $f\text{CO}_2$ in the OA community? We briefly checked this by going through papers which cited the Kim and Lee (2007) and Hernandez-Ayon et al. (2007) papers (ISI, accessed 5.07.2012;). From 10 papers citing Kim and Lee and 7 papers citing Hernandez-Ayon et al. (2007) only two papers consider the effect of DOM-Alkalinity on the computation of $f\text{CO}_2$ (Hunt et al. 2011, submitted to BGD after our work, and Hofmann et al., 2011, Ann. Rev. Mar. Sci. 3, 93ff). For the period 2009 to 2012 ISI reports (accessed 5.07.2012) a total of 942 papers for the key word 'ocean acidification'. It is beyond the scope of this rebuttal to access how many of these studies report experimental work in which $f\text{CO}_2$ was computed from A_T and C_T . In our paper we estimate from Nisumaa et al. 2010 that about 50% of OA studies in the past used A_T and C_T to compute other components of the CO_2 system. Arbitrarily assuming that perhaps half of the OA papers dealt with experimental studies applying such computations, one could speculate that up to 250 studies computed variables like $f\text{CO}_2$ from A_T and C_T , while at the same time only two papers consider this a potential problem.

Furthermore, we took a brief and qualitative look into whether OA researchers consider that computed $f\text{CO}_2$ has an uncertainty at all. Starting from the EPOCA web page (experimental data, individual experiments) we checked into paper published in Biogeosciences (29) whether they use $f\text{CO}_2$ as a master variable (12). In all of the latter studies $f\text{CO}_2$ was not measured but computed from A_T+C_T or $A_T+\text{pH}$. While all studies give an estimate of the uncertainty of the input parameters (A_T , C_T or pH) only two report an estimate of the uncertainty of computed $f\text{CO}_2$ (likely from error propagation).

Making the problem explicit, like in our paper or the recent work by Hunt et al. 2011 (BG), may help to build up awareness of potential issues of $f\text{CO}_2$ computations

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and stimulate scientists to invest time and effort in appropriate means, e.g. over-determination of the CO₂-system in their experimental systems.

Comment: 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 pK° 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?

Answer: For the choice of the 'default' pK in our experimental CO2SYS-DOM we were guided by e.g. the work of Millero et al. 2002 (Deep-Sea Res. I, 49, 1705ff; see their section 9) which assumes a pK of 4 for organic acids/bases. The functional group in mind is the carboxyl group. In order to be more consistent with the standard seawater model and the definition of alkalinity of e.g. Dickson, 1981, we have recoded CO2SYS-DOM and use now a default pK value > 4.5 . The procedure chosen is explained in much more detail in the revised version of the ms, see section 3.2. There, we also discuss at more length Fig. 6 which explicitly presents the sensitivity of $\Delta f\text{CO}_2$ with respect to the choice of the pK_{Org} . Results from this figure were included but only briefly mentioned in the BGD version of the ms. Changing the default pK_{Org} value in

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CO2SYS-DOM had no visible effect on the figures presented.

Comment: *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 $f\text{CO}_2$. 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 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).*

Answer: We agree that experiments where rapid phytoplankton growth takes place may be considered the most prominent examples where DOM-alkalinity may compromise computed $f\text{CO}_2$ values. However, for other experiments the source of the water used may be also an issue. E.g. water sampled just after a spring bloom from coastal regions may contain large amounts of DOM and potentially show a DOM-alkalinity effect (see comment by Tyrrell, 2010). Over the time of the experimental manipulation, such an effect may not be constant, e.g. due to biological degradation of DOM, formation of TEP, etcpp. Hence the background concentration of DOM and its potentially related effect of DOM-alkalinity on the computation of $f\text{CO}_2$ may change during the experiment. Only the over determination of the CO_2 system in a larger number of OA experiments will help to clarify whether the observed effect in the experiments reported here is a rare case or not.

Comment: *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. **Answer:** A more detailed description of the changes made in CO2SYS-DOM is now given in the rewritten section 3.2. Here we also explain in detail how DOM alkalinity is computed from an assumed pK , the pH and the prescribed potential DOM-alkalinity. We now also discuss in more detail Fig. 6 of the original manuscript which

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highlights the sensitivity of the effective DOM alkalinity to our choice of the pK_{Org} .

Comment: *Line 26 (p. 3804): Please define your Δ values, e.g. "wrong - right".* **Answer:** Our general usage of Δ values is introduced and defined in the introduction and follows examples from the published literature discussion CO_2 -system over determinations from the open ocean. In section 3.2 we compute ΔfCO_2 against the imposed fCO_2 as the reference. This is stated now more explicitly in the manuscript.

Comment: *Line 8 (p. 3805): Should reference be to Dickson et al. (2007)?* **Answer:** This section has been rewritten and the line is deleted.

Comment: *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)* **Answer:** The symbol for free hydrogen ion concentration is used more consistently in the final version of the paper and we will double check the final .tex produced by copernicus staff for BG for consistency of styles.

Comment: *p. 3807: borate (line 4) ; ellipses (not eclipses) (line 14)* **Answer:** Corrected.

Comment: *p. 3810 : "Gulf of Californi", not "California Bay", though similar phenomena were seen in San Diego Bay, and in San Quintin Bay (Hernandez et al., 2007).* **Answer:** Corrected.

Comment: *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.*

Answer: We expect a large variability of bulk DOM concentrations and DOM-alkalinity in coastal waters. Open coasts which are well flushed with open ocean waters will likely be dominated by the open ocean conditions, i.e. will be characterized by little

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DOM-alkalinity and its effect on computing $f\text{CO}_2$. Extrapolating from the few studies reporting a difference between measured A_T and computed A_T from coastal seas is agreeably difficult. However, we think we were careful already in the BGD version to write that based on the evidence presented 'we **speculate** that $\Delta f\text{CO}_2$ in coastal waters may at times be significantly larger than in open ocean waters'.

Comment: *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).* **Answer:** We assume this comment refers to p. 3812, line 23. We agree that the Hoppe et al measurements have been carried out prior to laboratory growth. However, nothing is known about the pre-sampling history of the water used by Hoppe et al. which came from an environment known for its seasonal DOM fluctuations. However, we agree with the reviewer that it is speculative whether DOM-alkalinity effects contribute to the Hoppe et al. observation. We will rephrase the sentence respectively.

Comment 1 (J.P. Gattuso)

Comment: *The contribution of Koeve et al. (2011) is important because it could have serious implications on the set-up of ocean acidification experiments. It is critical that the potential problem of using CT and AT to estimate $f\text{CO}_2$ is re-assessed in the context of perturbation experiments. The problem of using AT when the DOC production is high is briefly mentioned in the "Guide to Best Practices on Ocean Acidification Research and Data Reporting" (Gattuso et al., 2010) and a more extensive coverage may be needed in a subsequent edition.*

I just want to highlight the fact that the potential discrepancy that is described by Koeve

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et al. (2011) is perhaps not very widespread. The reason is that phytoplankton perturbation experiments often use diluted cultures and benthic perturbation experiments often use open-water systems. In both cases there is either little or no accumulation of DOC. It would be useful to estimate the number of experiments published to date that are potentially affected.

Answer: It is beyond the scope of this work to evaluate individual published papers presenting experimental OA work or even to provide a review of how reliable computed $f\text{CO}_2$ in published studies has been. This is simply for the reason that such papers usually do neither report DOM data nor sufficient CO_2 system data. As discussed in our paper, there is currently a very limited number of OA experiments which present an overdetermined CO_2 -system, i.e. that measured more than just two CO_2 -system variables. Such data are, however, the fundamental basis to answer the question of Prof. Gattuso. For the future, we proposed, based on the results of our study, that OA experiments overdetermine the CO_2 system in order to make sure that in particular $f\text{CO}_2$, which is often used as a master variable in OA research, is fully reliable. Finally, a larger set of experiments with overdetermined CO_2 -system available hopefully in the future should also allow to answer the question on how reliable computed $f\text{CO}_2$ from early OA experiments has been.

Comment 2 (C.W. Hunt)

Comment: *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.*

Answer:

Comment: *GENERAL COMMENTS:*

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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 $f\text{CO}_2$ 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 CO_2 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 $f\text{CO}_2$ 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 $f\text{CO}_2$ including DOM diverge significantly from those which do not. It is instructive, however, to see how this affects $f\text{CO}_2$ 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.

Answer: Concerning the open ocean there are a number of studies which report overdetermined CO_2 -system datasets. These studies generally find good agreement

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of measured and computed variables and hence suggest that organic acids and bases are not likely an important issue for the computation of e.g. $f\text{CO}_2$ from A_T and C_T . The computational error (i.e. $(\text{meas.}-\text{calc})/\text{meas.}\times 100$) is usually below 5% (see the introduction for references). The most explicit treatment of organic acids/bases can be found in the work of Millero et al., 2002 (Deep-Sea Res. I 49, 1705ff) which explicitly discusses the possible role of organic acids/bases as uncertainty for computing $\Delta f\text{CO}_2$ in open ocean data. Given that their errors are much smaller (s.a.) than compared to those we observed in our experiments, they find, similar to our study, that $\Delta f\text{CO}_2$ increases with $f\text{CO}_2$ and may be explained by assuming a constant organic acid concentration of 8 $\mu\text{mol/kg}$ and a pK of 4. Concerning rivers, estuarine and coastal waters, the few available studies (see discussion in our paper) indicate to us that incomplete chemical seawater models may be of more concern there. This is in agreement with often reported higher concentrations as well as seasonal fluctuations of bulk dissolved organic matter in these waters.

Comment: *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.* **Answer:** We thank the reviewer for critical and careful reading of the manuscript.

Comment:

TECHNICAL COMMENTS:

Methods:

The authors specify that T_A 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 T_A analyses contribute to alkalinity? This seems to be a poorly understood topic, but there must be

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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.

Answer: The potential role of particle surfaces as contributors to A_T has been discussed elsewhere based on dedicated experiments (see Kim et al., 2006, Limnol. Oceanogr. 5, 331ff). We didn't want to repeat this discussion in this paper. But we agree with the reviewer that in particular in experimental system, but also in e.g. coastal water which are often characterized by high particle loads, organic particles can constitute a significant additional problem to the computation of fCO_2 if based on A_T (from unfiltered samples) and C_T . We will explicitly mention the intention of filtering A_T samples in the methods section. We will also include respective concerns in the conclusion section. It is noteworthy that we have not seen many OA papers reporting whether A_T samples have been filtered or not. In some of the studies this may constitute an additional limitation to the reliability of computed fCO_2 from past experimental studies.

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.

Answer: Details of the A_T methodology will be added to the final version of the paper.

Comment: *Results:*

It would be helpful to explicitly state the a positive ΔfCO_2 indicates that $fCO_2(CT-pH)$ is higher than $fCO_2(TA-pH)$. The notation of ΔfCO_2 is a little confusing in that respect: a positive ΔfCO_2 means that the 'real' fCO_2 is actually lower than the $fCO_2(TA-pH)$.

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Answer: When computing our Δ values by including a term (reference - calc) we follow examples from the published literature on overdetermined CO₂-system from the open ocean, e.g. Lee et al., 2000, Millero et al., 2002. We agree that using a term (calc-reference) might be more straight forward, but we decided to use a term introduced in the respective literature.

Comment: *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.*

Answer: We have rewritten section 3.2 and provide now more details on the modifications of our experimental version of CO2SYS. Also, CO2SYS-DOM will be made available to the public via the GEOMAR repository upon the publication in BG.

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

Answer: Considering claims by other reviewers that this paper does not provide much new information, we hesitate to reproduce even more of what has been said elsewhere by some of us.

Comment: *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.*

Answer: We agree. We now give an equation 1 presenting the standard definition of seawater alkalinity in the introduction already. In general, we have reorganized section

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3.2 to a large extent in the final version for BG.

Comment: GRAMMAR AND SYNTAX

P3798 L6, remove 'there' **Done.**

P3799 L16, rewrite "requires to perform.." **Done.**

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. **Sentence deleted.**

P3799 L19, "have significantly developed through the recent two decades" improper syntax **Rewritten.**

P3799 L24 (and throughout manuscript), "measurements where available" the correct word to use in this situation is 'were', not 'where' **Done.**

P3800 L1, remove "in a discussion paper" **Done.**

P3800 L6, "where" should be "were" **Done.**

P3800 L18-20, Confusing sentence. **Rewritten.**

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? **Usage of DOM vs. DOC in the paper has been streamlined. See response to A. Hofmann for more details.**

P3803 L13, $\Delta[\text{CO}_3^{2-}]$ decreases in Fig.2. **Rewritten.**

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

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as CO2SYSDOC. The first three paragraphs of the "A Model Experiment" section could use a rewrite, they are pretty hard to follow. **This has been improved, section 3.2 has been restructured and reworded.**

P3805 L6, Change "behaviour" to "behavior" **Changed.**

P3805 L7, Change to "specifically" **Changed.**

P3805 L18, remove "Obviously", rewrite to "When CT and pH are used as input variables (Eq. 1). . ." **Rewritten.**

P3806 L7 and throughout, "eclipses" should be "ellipses" **Done.**

P3806 L18, "requires to first" change to "first requires an estimate of the hydrogen. . ." **Rewritten.**

P3807 L4, change to "total borate, fluoride, and sulfate" **Rewritten.**

P3807 L18, change "a wrong pH" to "an inaccurate pH" **Rewritten.**

Answer: We thank the reviewer for careful reading and his corrections.

P3808 L11, can you give a percentage of the "minor contribution" of the choice of constants? **Answer:** This will be explained in more detail in the final version of the ms.

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

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