

Interactive comment on “Biogeochemical processes and buffering capacity concurrently affect acidification in a seasonally hypoxic coastal marine basin” by M. Hagens et al.

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Received and published: 7 January 2015

In this work, the authors presented a very nice research on the seasonal variation of pH and oxygen dynamics in the water column of a seasonally stratified coastal basin. Their work also highlights that process rates, buffering capacity and ambient pH are all essential compartments when determining the vulnerability of a system to changes in pH. It will have a real impact on the field of coastal ocean acidification research in the context of interactive effects between ocean acidification and eutrophication. The manuscript was generally well prepared (but see the one note below). As far as I can tell, there is no technical error (but see comments below on points that may need

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clarification). Thus, I support the publication of this ms with minor revision.

Major concern one. The authors assume that all readers are somewhat familiar with the proton cycle and budget approach, the buffer capacity defined here and the Hoffmann papers. This is actually not the case. Some explanations and warning are needed early in the paper. When I first read it, I took the proton production and consumption defined in this paper as equivalent to the traditional TA production and consumption (with opposite sign). My uneasiness grew I read further. When I came to line 11, p. 15842 (between eqn R1 and eqn 7), I realized the way H_3PO_4 coefficients are formulated indicates a difference reference point than the traditional TA definition. Thus I stopped and went back to read the Hoffmann et al. 2010 (Mar Chem) paper. I appreciated the beauty of the approach immediately and agreed this is a good and the right approach. (not sure if this is the place to express my apology to Andreas for not trying harder to understand his paper when I first saw it a few years ago).

The point is many people, like me, thought they know what the Hoffman approach is; but they probably don't. Some text is needed earlier to say the advantage of the Hoffman approach rather than simply doing the traditional DIC/TA approach. I feel a paraphrase of what was said in Hoffman et al. (2010, section 3, p. 248) will help: “when multiple biogeochemical processes are acting concurrently, only the combined effect of all processes on pH can be calculated, one cannot quantify how strongly individual processes influence proton cycling.”

The above said, I can write in length to defend and list the advantages of the traditional approach of using a combination of DIC and TA as well as the practicality of the Hoffman approach (I need to and will apply it to a real case before I am fully convinced). Since it is already nearly 7 pm in the last day of the open review period, I better move on.

Major concern two. “The sum of dH/dt (total) of all measured processes was 1–2 orders of magnitude higher than $\text{dH}/\text{dt}(\text{obs})$. As a result, the budget closure term dominated

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the proton cycling intensity.” So I feel this point, plus the fact that H⁺ is turned over rapidly among various processes, would make it very hard to verify the model results. Some discussion of uncertainty will help.

The rest of notes are all very minor and it is up to the authors to take or ignore them. I do not feel figure 1 to be very informative. It gives a general picture but not much details about the sample sites. For example, one cannot tell where is the connection to the north sea and where are the two sills at the landward and seaward. And where are S1, S2, and S3? What exactly is a sluice? From fig. 2, it appears it can be closed or open to variable depths. (I see it is explained later in section 3.1) p.15830, line 22-23, I believe the first part of the sentence is correct (an effect that is most pronounced in eutrophied waters), but the last part is incorrect (at relatively high temperatures and salinities) I assume you do not mean that the effect is most pronounced “in high temp and high salinity waters” (which is incorrect and is not what Sunda and Cai’s paper says), and that you simply mean the example Sunda & Cai give is “at relatively high temperatures and salinities.” So please modify the sentence.

p.15841, line 1. Since your samples dates have lower wind speed than average, the calculated air-sea CO₂ flux could be lower than real. I suggest you use monthly averaged wind speed plus a non-linear coefficient (Jiang et al. 2008 JGR-Ocean). In the context of examining monthly evolving of CO₂ system parameters, I feel this most appropriate. But it probably won’t make too big a difference; so up to you. —Jiang, L.-Q., Cai, W.-J., Wanninkhof, R., Wang, Y. and Lüger, H., 2008. Air-sea CO₂ fluxes on the U.S. South Atlantic Bight: Spatial and seasonal variability. J. Geophys. Res., 113(C7): C07019.

p.15848, line 21, the word “strongly” probably should be replaced with “greatly.” It is better to put the description of DIC variation in the context of salinity unless some kind of normalization is applied (nDIC). Otherwise, we have no idea how much change is due to mixing (or lateral transport).

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p.15848 and p.15849, same. a description of TA distribution (in particular the surface bottom difference) without in the context of salinity doesn’t provide much meaning information. Thus, I feel this part can be shortened.

In p.15849, line 21, the word “drawdown” is a misuse (it is simply a shift of equilibrium of CO₂, which is converted to HCO₃⁻); thus simply say low T led to a low pCO₂ would be better. Why pCO₂ build-up had a time delay (is behind) of DIC build-up? Hope you will explain this in the Discussion.

In p. 15850, line 8, can’t you just say “as expected, TA had no significant correlation with. . .”? Isn’t that something we would expect?

p.15861, while the conclusion derived here is correction, do we really need the lengthy discussion in p.15861 (lines 7 to bottom) to derive the conclusion? I would say this is true for any natural water. We know pH in seawater is controlled (buffered) by weak acid-base (mainly the carbonate system) thus proton production/consumption is rapidly supplied and taken away by the various acid-base equilibrium reactions. We simply know this. (maybe I am wrong)

p.15863, “neither does it not show a clear pattern with TA”? (is this correct?)

The conclusion drawn at the end of A2 is puzzling—calculated pCO₂ is higher than measured. If there is additional base inside the TA (DOM for example) and our acid-base model doesn’t include it, then we would expect a lower calculated pCO₂ (the TA used in the calculation is too high). Now since the calculated pCO₂ is too high, I can only conclude that your TA is too low, assuming your DIC has no problem. You also mentioned that this happened to samples below the pycnocline. Okay, I think I have an answer—your waters have high NH₄ concentrations. NH₄ was then oxidized during sample storage or titration, thus leading to a lower TA. But what I don’t understand is those samples with highest pCO₂ values (they should be from bottom waters) have lower calculated pCO₂. Why?

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