Biogeosciences
Discussions

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Interactive comment on "The impact of sedimentary alkalinity release on the water column CO$_2$ system in the North Sea" *by* H. Brenner et al.

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This work is probably the first to discuss the role of benthic TA flux (and DIC flux) on CO2 uptake from the atmosphere based on specific field measurements. I think it will be a good contribution to our understanding of the issue and will help to improve more complicated system level models (such as physical-biological coupled ROMS models). Many scientists talked about how benthic TA (or river TA) would enhance coastal ocean's ability to take up CO2 from the atmosphere or the coastal ocean's buffering capacity. They often forgot that the discussion should be put in a context of the ratio of the TA input to the associated DIC input. This paper considers the DIC and

TA budgets simultaneously. Towards the end of the paper (together with Fig. 12), it correctly pointed out âĂŤ"The direction of a CO2 flux between the surface water and the atmosphere is determined by the pCO2 gradient between water and atmosphere, which is ultimately governed by the ratio of internal DIC over internal AT release." I think this point should be brought out earlier and be emphasized in the introduction. I support the publication of this paper with minor revisions. The notes, below, I wrote down whiling reading the ms are meant to help the authors to present the work more clearly and to be easier to understand to general audience (you would like to see people outside sediment diagenesis to understand it). I do not need to read the revision again but trust the senior author be the gate keeper.

The only other major issue I have is noted here: p.12419, line 23-25, I am a bit confused here where did you measured or assumed denitrification rate before this point. If not, which number do you take to scale (X1/0.8) the rate down to1.89 mmol/m2/d? p.12421, line 12 to the end and Table 5. I am confused here, how did you derive the rates of various diagenetic processes listed in Table 5? Your only data are benthic fluxes of O2, DIC and TA. No benthic flux or porewater concentration profiles of nutrient, DIC-C13, or Ca2+, etc. No bottom concentrations either. What data do you use to constrain the steady state diagenetic model? You have some explanations to do here. Based on my knowledge of this group's past work, I am confident they must have all the initial and boundary conditions and rates that allow them to run the sediment model and derive the above rates. But I do not see these in the paper and they need be presented clearly.

Minor-moderate comments

Introduction

You may want to cite Bauer et al. 2013 in "and between 10 and 25% of the current day oceanic CO2 uptake (Regnier et al., 2013; Liu et al., 2010)." Bauer, J.E., Cai, W.-J., Raymond, P.A., Bianchi, T.S., Hopkinson, C.S., Regnier, P.A.G., 2013. The changing carbon cycle of the coastal ocean. Nature 504, 61-70.

The first to point this out was in Cai et al. 2006–"In general, most open shelves in the temperate and high-latitude regions seem undersaturated with respect to atmospheric CO2, while the low-latitude shelves generally tend to be supersaturated (Chen and Borges, 2009)."

Like this approach–"Here we used two different stirring rates at each station to mimic a range of interfacial pressure gradients and solute exchange conditions"

Are you sure you are using 10 mL of sample for DIC analysis? "DIC was determined using an AS-C3 DIC analyzer (Apollo SciTEch, USA), in which the sample (10 mL) was acidified and the released CO2 was detected using a solid state infra-red CO2 detector" As far as I know, the sample volume for one analysis is 0.7-1.0 mL.

Section 2.5, Not clear what is this diffusive condition? Was the overlying water slowly stirred? "Profiles were measured under di_usive conditions and the slope d[O2]=dz was determined from the gradient in the diffusive boundary layer (Glud, 2008)."

Results Not sure if Figure 2 is necessary.

3.3 Line 18, I find it hard to accept the concentration changes with time during a few hours of incubations as "temporal evolution." Find a better term. "temporal evolution" should be reserved for time course observation of at least a few seasons and perhaps longer in a natural setting such as an entire bay or at a time series observation site.

Fig. 4b is not needed. Simply say it is sufficient as there is no correlation for readers to examine.

Discussion 4.1, when you talk about TOU, you should mention under which stirring scheme (40 or 80 RPM) as rates are 80% greater under the latter condition.

p.12411, lin e 17-21, Such argument on the correlation of benthic flux to water depths was made years ago (for example Jahnke's or Reimers work offshore California). Don't forget, sediments at deep depths also accumulate much slower, allowing OM to be decomposed at the sediment-water interface (not necessarily in water column). So it is

not necessarily because of water depth.

4.2 and 4.3 I am a bit puzzled by the less consistent treatment of DIC flux and TA flux. 1) Not sure why this entire story of Ra isotope based porewater exchange rate was only applied to TA flux not to DIC. 2) Is the discussion on RQ of 0.77, being Redfield (in 4.2), meaningful in the context of sources lead to TA production (4.3)? This issue need be addressed. Later you stated, "The most dominant AT producing reaction is carbonate dissolution, followed by sulfate reduction and denitrification." So, explain why we are even expecting the ratio of DIC/O2 benthic fluxes to be similar to the Redfield RQ?

4.4, at the end of discussion aerobic processes (respiration plus NH4 oxidation), you should point out the "bottom line" that net TA/DIC (or TA/O2) production/consumption ratio is -17/106 (or -17/132). While I like your way of presenting eqn 5 and eqn 6 separately, this net result need be emphasized (said).

While there is no error in presenting the diagenetic equations and the associated proton and TA balance, I felt they are at least not consistent. You present DIC as CO2 not as HCO3- but TNH4 as NH4+ and P as H2PO4- (as dominant species). Wouldn't it be easier to use only undissociated form of species to assess TA gain per model of OC decomposition (for example, see Cai et al. 2010)? Of course it is your choice and it does affect the results. Cai, W-J., Luther, George W. III, Cornwell, Giblin, Anne E., 2010. Carbon cycling and the coupling between proton and electron transfer reactions in aquatic sediments in Lake Champlain. Aquatic Geochemistry. 16:421-446, DOI 10.1007/s10498-010-9097-9.

Section 4.4 p.12419, line 23-25, I am a bit confused here where did you measured or assumed denitrification rate before this point. If not, which number do you take to scale (X1/0.8) the rate down to 1.89 mmol/m2/d?

p.12421, line 12 to the end and Table 5. I am confused here, how did you derive the rates of various diagenetic processes listed in Table 5? Your only data are benthic fluxes of O2, DIC and TA. No benthic flux or porewater concentration profiles of nutrient,

DIC-C13, or Ca2+, etc. No bottom concentrations either. What data do you use to constrain the steady state diagenetic model? You have some explanations to do here.

4.5, I think you mean does NOT in this sentence "An efflux of AT from the sediment does <NOT> necessarily result in an increase of AT whole system, as in the water column, some biogeochemical processes are opposing the AT generation in the sediment."

Do you even need eqn 15, which is just opposite to the 14? I don't think so. Delete.

p.12425, line 1 (above eqn 17), move "the" before "combined"

4.6, I am glad you said this clearlyâĂŤ"The direction of a CO2 flux between the surface water and the atmosphere is determined by the pCO2 gradient between water and atmosphere, which is ultimately governed by the ratio of internal DIC over internal AT release" But then in the next sentence why I do not see anything regard DIC flux?âĂŤ" As shown above, the net generation of alkalinity amounts to 2.0 mmolEq/m2/d, and hence, 1.70 mmolC/m2/d of CO2 can be taken up." (you mentioned river OC-derived DIC) Is this because there is no next internal DIC generation? I now see there is a large DIC efflux out from the sediment, which is only to balance the DIC loss to the Rpp term in water column. I think the explanation can be clearer. Another issue is that the whole conclusion (regarding the role of benthic TA flux on CO2 uptake) would also rely on the assumption F(DIC)out = F(TA)out.

Right before I submitting this (read again), I noticed you have a different unit for TA and DIC. They should be the same, both in mmol. The unit Eq was abolished by IUPAC many decades ago. (thus for TA, it is the mmol of HCl used to titrate the water to the CO2 equivalence point)

A few additional minor points (from one of my students), pg 12405 line19 The word between is repeated pg 12406 lines 14-16 There is a comparison of porosity yet no value is given for the SKNT stations. pg 12406 paragraph starting on line 18 There are too

many acronyms, making it hard to follow. pg 12410 Are there newer studies than 1993 and 1998 to compare the TOU too? I also feel that bottom water temperature is a larger controlling factor on TOU than depth. Therefor, I would begin with the temperature discussion and talk water depth second. pg 12411 line 8 change colder to cooler and add what it is cooler than. Sentence starting on line 9 make more direct, delete the use of 'hence'. The paragraph on line 15 would be better served having the discussion of water depth in the paragraph before than the discussion of water temp. pg 12417 line 26 The assumption that the overlying water is still always oversaturated with carbonate from research published in 1998 (17 years ago) is probably ok, but with the change in atmospheric CO2 over the last 17 years makes me question if oversaturation continues year round.

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