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.
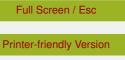
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We thank the reviewers for their useful comments and have revised the manuscripts accordingly.
Response to reviewer comments by Wei-Jun Cai

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.

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Reference added

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)."
Reference added

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.
The sample volume was 10 ml of which 0.8 mL was introduced into the AS-C3. Manuscript updated.

Section 2.5, Not clear what is this diffusive condition? Was the overlying water slowly stirred? "Profiles were measured under diffusive conditions and the slope d[O2]=dz was determined from the gradient in the diffusive boundary layer (Glud, 2008)."
The water tank was constantly bubbled with air, to ensure a constant water flow over the sediment surface, and so a proper diffusive boundary layer. Method section updated.

Results Not sure if Figure 2 is necessary.
We decided to keep figure 2, as it illustrates the different stratification regimes in the three parts of the North Sea, which were subsequently considered as geographical subregions of the North Sea system.

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
Text revised as suggested.

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

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.
All TOU rates presented in the following section are not subdivided between both stirring speeds, but discussed together. A statement has been added to the manuscript.

p.12411, line 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
While this statement is generally true, it has liitle relevance to our study as the North Sea is generally a non-deposition system. Besides an area in the Norwegian trench, no sediment accumulates in the North Sea.

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?

(1) The only other study that has studied Ra effluxes in the North Sea (Moore 2011), only sampled A_T. We used this study to compare all aspects of the method (pore water [Ra], pore water volume exchange, pore water $[A_T]$). Sin no prior data on DIC effluxes was available, we did not discuss it.

(2) We use the RQ as an indicator for the degree of reoxidation of reduced species associated with anaerobic remineralization. The RQ of 0.77 serves thereby as a reference baseline of aerobic respiration, and not as a prediction of expected DIC/TOU ratios in this study. A clarifying statement was added to the manuscript.

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).

Text has been revised as suggested.

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.

We chose to systematically represent the acid base species in the reaction equations according to their "zero level of proton" - see definition by Wolf-Gladrow 2007. This way the proton production/consumption in these reactions equations represents the alkalinity consumption/production. As a result, the alkalinity effect is directly visible from the proton stoichiometry in the reactions equations.

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 to1.89 mmol/m2/d?
We scale the denitrification rates based on the nitrification rate and assuming 20% of the total denitrification rate is fueled by external nitrate. The nitrification rate is introduced in the section before. The nitrification rate has now been added in this section.

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.
We used a combination of literature values and our measured fluxes of O_2, DIC and A_T to constrain the different reaction rates. Details on the calculation of each reaction rate are discussed in section 4.2. For a better understanding, links to that section were added in the text as well as in the table caption.

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."

Text revised as suggested.

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

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

4.6, I am glad you said this clearly AT "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. 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.
The section has been rewritten to clarify our reasoning.

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)
Units for A_T have been changed as suggested.

A few additional minor points (from one of my students), pg 12405 line19 The word between is repeated pg 12406 lines 14-16
Text revised as suggested.

There is a comparison of porosity yet no value is given for the SKNT stations.
Values for SKNT are added.

pg 12406 paragraph starting on line 18 There are too many acronyms, making it hard to follow.
All acronyms used in that paragraph are often used throughout the whole manuscript and half of them are very commonly used in other studies. Therefore, we do not expect readers to get confused by using them in this paragraph.

pg 12410 Are there newer studies than 1993 and 1998 to compare the TOU too?
A more recent study was added as a reference.

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.
We decided to keep the order, as water depth directly affects the temperature in the bottom water.

pg 12411 line 8 change colder to cooler and add what it is cooler than.
Text revised as suggested.

Sentence starting on line 9 make more direct, delete the use of 'hence'.
Text revised as suggested.

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.
See comment above.

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.
A more recent study was added as a reference.

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