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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.

H. Brenner et al.

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Response to reviewer comments by J. Paetsch

General/major comments:
The authors use mean values of strongly spreading data. They should discuss the sensitivity of their budget in relation of the (mean) input data.
The revised manuscript includes a discussion of the sensitivity of R_{min} towards the A_T budget. A graph visualising the sensitivity of A_T towards R_{min} was also added.

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Very strong assumptions and "guestimates" were made (steady state, Rmin,..). They must be justified and discussed in more detail. I will pinpoint these items in my detailed remarks.
Replies are included under the different remarks below.

There are faults in Tab. 5 and even in the equations ((7) and (9)). Most of them do not change the authors' overall statements. I think parts of the conclusion must be rewritten when the bugs are fixed. I will give a recalculated table 5.
The original table 5 contained a few errors, as values were not correctly transcribed from teh model output. The rate for DNF was given in the wrong unit and subsequently also the A_T change was miscalculated. These errors are fixed in the current table. However, our model did not include any errors (we rechecked all equations and associated R scripts). We do not agree with the model expressions for AR, SR, IR , PF, SO and TOU as proposed by the reviewer (and hence with the associated rate estimates). Consequently, we also do not agree with the assessment of the reviewer regarding the relative importance of the different elemental cycles for the A_T turnover.

The impact of sedimentary alkalinity flux on pelagic DIC dynamics does not take into account the simultaneous sedimentary DIC flux, even though the authors claim this.
Our calculation does account for the sedimentary DIC release. We have now rewritten section 4.6 to clarify this. The net generation of alkalinity amounts to 2.3 $mmol\ m^{-2}d^{-1}$. Similarly the net generation of DIC amounts to 1.0 $mmol\ m^{-2}d^{-1}$. As we assume that organic matter burial is negligible, there is no net internal *net* DIC generation due to respiration of locally produced organic matter (the respiration of autochtonous organic matter in both water column and sediment matches the primary production of autochtonous organic matter in the water column). However, as noted above, riverine input of organic matter, and so, respiration of this organic matter releases 1.0 $mmol\ C\ m^{-2}d^{-1}$ of DIC. The internal release of 2.3 $mmol\ m^{-2}d^{-1}$ of A_T

and 1.0 $mmol\ C\ m^{-2}d^{-1}$ of DIC, will eventually lead to an 0.96 $mmol\ m^{-2}\ d^{-1}$ of of CO_2 from the atmosphere.

The authors compare their summer fluxes with annual fluxes. It is known that summer fluxes are the largest all over the year. They must discuss this point and give the reader hints about this problem at all places in the text where this occurs.
Throughout the manuscript, we tried to compare our June/September values with the best fitting literature values. When available, we used previously published values for Summer/Autumn (e.g. A_T generation as calculated in Thomas 2009. In those cases that seasonal data were not available, the manuscript was updated to remind the reader of the seasonality of the dataset.

The title is misleading as it reflects only the last chapter. I suggest something like "North Sea wide pelagic-benthic flux measurements of Alkalinity, Dissolved Inorganic Carbon and Oxygen and their impact on..".
We decided to keep the current title, which is more concise. Our manuscript deals with both flux measurements as well as the construction of an A_T budget for the SNS, in order to finally calculate the impact of sedimentary TA release on atmospheric CO2 uptake. We think that the current title suitably covers this story line.

The unit mmol Eq should be replaced by mmol C
This is now changed throughout the updated manuscript.

Detailed remarks:
P12396 L14 ".. should be considered as an important factor"
Text revised as suggested.

L21 Liu et al 2010 never discussed shelf uptake

Reference deleted.

P12397 L8 ".. the question .. which particular drivers ..
Text revised as suggested.

P12399 L4 Pätsch and Kühn 2008 used the 50 m depth contour to separate SNS and NNS. So your definition of SNS is very special. Perhaps you can use another acronym?
In absence of better alternatives, we keep the used acronyms, but updated the manuscript to ensure that no confusion about the delineation of the SNS and NNS arises. We also now explicitly mention the SNS surface area that was used in our calculations

L29 "is the only net outflow .."
Text revised as suggested.

P12400 L2 ".. by strong .. currents.."
Text revised as suggested.

L12 " .. and near Helgoland in the German Bight (Hebbeln et al., 2003)"
Text revised as suggested.

P12404 O2 and pH microprofiling: Please give an estimate of the accuracy of the profiling data. I guess you took these measurements on board. The movement of the ship might have impacted the quality of the measurements. Could you please comment on this?

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Accuracies for O_2 and pH microprofiling were added. Additionally, to minimize the error by ship movement, the microprofiling setup was placed in the center, the most stable spot, of the ship. A respective comment was also added.

P12405 L15 Fig. 2b: Station 11 cannot have a depth < 500m. Fig.. 2c there is only one profile displayed.
These were indeed errors. Figure 2b showed the temperature profile for station 65 (and not 45), thus the < 500 m depth. Figure 2c only displayed the temperature profile of station 80 (and not 65). The caption of figure 2 was changed accordingly.

L21-22 Could you show this
Bottom water O_2 shows no correlation between different regions. We don't think its necessary to emphasize this using a scatter plot.

P12406 L3 the minimum median grain size of 21 mum cannot be found in Tab. 1
Station 88 exhibits a median grain size of 21 μm. Correct value is added to table 1.

L3-4 Do really both areas exhibit the same (215 mum) mean median grain size?
The median grain size for stations of the SNS is 249 μm. Text revised accordingly.

L10 22 mum cannot be found in the table. Please also add acronyms into Tab. 1 to identify the membership in SNS, SKNT and NNS
The correct value of 21 μm was added in the text and table 1. Column with regions added.

L19 Which criterion did you use to determine the representativeness?

Stations were chosen to represent average benthic fluxes for the respective region of the North Sea. Hence, e.g. station 20 located in the German Bight was not considered, as most likely, sediments in this region are more active in terms of respirations rates than sediments of the remaining, major part of the SNS. Manusript updated by a comment pointing that out.

L22 What is the difference in the numbers of subsamples? It seems that there is systematic noise at the DIC and TA data.
5 subsamples were taken per incubation. At least 4 were used to calculate solute fluxes. A comment to clarify that was added.

P12407 L15: In this case I do not know which correlation was tested.
The correlation between TOU rates at 40 RPM and TOU rates at 80 RPM was tested. Manuscript updated clarifying the correlation.

P12408 L10 and the following: Please give an estimate of the accuracy of the profiling data. I guess you took these measurements on board. The movement of the ship might have impacted the quality of the measurements. Could you please comment on this?
The microprofiling was setup at the most stable (center) part of the ship, the ensure most accurate results. In case of stronger winds, either microprofiling was not possible to carry out in order to prevent sensor damages or sediment sampling overall was not possible. Accuracies and comment about the quality of the profiling in regards with ship movement was added in the method section.

P12409 L1 give ranges or mean and stdv
Standard deviations for OPD added.

P12410 L29 " .. is the bottom temperature exhibiting a north – south gradient in summer, with higher temperatures in the south
Text revised as suggested.

P12411 L11 "a nearly doubling .."
Text revised as suggested.

L14 ".. compared to the SNS (Tab. 3)."
Text revised as suggested.

L14 Discuss the deviating TOU of station 38 and 45 (Tab. 3 and Tab. 1)
The water depth of station 38 and 45 is in both cases greater than the thermocline, thus lower bottom water temperatures are leading to TOU rates more similar to TOU rates of the NNS. A short discussion was added to the manuscript.

L17 I cannot identify a correlation between water depth and TOU, TA-flux, DIC-flux in Fig 6. Black and blue dots show more or less the same values. The red ones show almost all values for depth < 50m. Try to plot only the red dots with a higher depth resolution.
The correlations discussed in these plots are the correlations between water depth and TOU, A_T and DIC fluxes for all stations and regions combined. Thus, we cannot remove points from the NNS and SKNT of these plots. Furthermore, we would like to point out that these parameters are tested for any (including non-linear) correlation. Thus, we decided not to change figure 6.

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L24 Are porosity and grain size dependent on (or correlated with) depth? If this is so, you should use only probes with similar depths for checking the correlation between porosity/grain size and TOU and TA/DIC fluxes.
Porosity and grain size correlate indeed with water depth. However, the sole purpose of figure 6 is to test for correlation between parameters. For this, parameters do not require to be independent from each other.

P12412 L4 "The importance of wind and tidal induced advective transport (at station 11) ..(Fig. 5a). This is reconstructed by the strong .."
Text revised as suggested.

L16-L20 "A second .. determined" this sequence should be canceled.
We think this section is relevant (exclusion of O_2 profiles influenced by advection), and so we did not delete it. This section provides the explanation for the possible occurrence of advective transport processes affecting the DOU rate measurement (as discussed below).

L24 This inverse relationship is based on the balance between the diffusive flux and the aerobic degradation with the assumption of steady state dynamics. Please help the reader to understand equation (3).
Manuscript updated.

L24 Fig. 7a does not contain empty circles
Caption of figure 7 updated.

L25 Is L the theoretical OPD?
Yes. "Theoretical..." added in the text.

L26 " , and [O2]bw is the oxygen concentration in bottom water"
Yes, manuscript updated.

L26 what is F0O2 in eqn (3)?
$F^0_{O_2}$ is the benthic diffusive oxygen flux. Manuscript updated.

L27 Fig 7b does not show the theoretical OPD from measured DOU. It shows the correlation between measured and theoretical OPD.
Text revised as suggested.

L27 Why is the number of red dots in Fig 7 so small?
At some stations, oxygen did not deplete over the measured depth (Table 3). Thus, at these stations, no OPDs could be measured based on oxygen microprofiles.

P12413 L1 The measured OPD is in two cases smaller than the calculated ones. Discuss this. For which stations is this true?
This it true for station 52 and 65, both stations of the SKNT. Both exceptions are now named in the manuscript.

L2 use "equation (3)" instead of "model 3"
Text revised as suggested.

L4 It is clear that non-diffusive transport increases the oxygen availability. You should discuss whether your DOU-measurements include some other than diffusive transport or input variables of eqn (3) are not chosen adequately.

Equation 3 excludes per definition any other but diffusive transport for DOU rates. See comment above.

L7 ff: You should refer to Tab. 2. In the text you should mention that the values in line 9-10 are mean values.
Text revised as suggested.

L16 Same as for TOU: Fig. 6 should be improved. The dependency of depth and grain size/porosity must be excluded.
Figure 6 shows pairwise correlations between different parameters. For this statitical analysis, it is not required that parameters are independent from each other. See comment above.

L19 "DIC-flux is correlated with TOU"
Text revised as suggested.

L20 Fig. 8b is called before 8a. Exchange 8a and 8b.
Figure 8a and 8b swapped.

L24 you mean Fig. 8b?
Now figure 8a.

P12414 L2 You mean Fig. 8b?
Figures swapped, now figure 8a

L8 "one mole DIC"

Text revised as suggested.

L10 “re-oxidized”
Text revised as suggested.

L13 “(Fig. 8a)”
Now figure 8b. Text revised accordingly.

L22 “is in good agreement..”
Text revised as suggested.

L23 “The disagreement (e.g.at station 38) ..”
Text revised as suggested.

P12415 L4 mention that these number are mean values.
Text revised as suggested.

L12 “(Fig. 8a)”
Now figure 8b. Text revised accordingly.

L26 more precise please. The recalculation of 131.2 Gmol from Tab. 1 in Thomas et al. (2009) yields 7.6 mmol d-1 m-2
131.2 Gmol as reported in Thomas et al. (2009) divided by the surface area of the SNS used in that paper (150392 km2) and this divided by 1/4 of the year (365.25/4) indeed yields 9.6 $mmol\ m^{-2}\ d^{-1}$. Note, that Thomas 2009 uses a different definition/surface area of the SNS than (Paetsch 2008). However, in the updated manuscript we use

both summer and autumn observations, as we think this is more accurate to be compared to values measured in June and September, which yield 8.0 $mmol\ m^{-2}\ d^{-1}$ alkalinity.

P12416 L16 "assumptions"
Text revised as suggested.

P12417 L1 "a high benthic respiration .."
Text revised as suggested.

L6-7 ".. invoke the question which processes are generating AT in the sediment"
Text revised as suggested.

L16 omit "now"
Text revised as suggested.

P12418 L15 please insert here an acronym for the flux, say fCD = ... Then you can recall this acronyms afterwards (e.g. in eqn (12))
We think it is important to keep the full names throughout the discussion and in table 5, to allow the reader to understand rates and fluxes based on one table alone. Thus, we decided not use acronyms for fluxes in the text .

L19 Make clear that OM is derived from eqn (1) in Paulmier et al (2009)
Text revised as suggested.

L26 Give a justification for the estimate Rmin = TOU. Why not taking the DIC efflux as

estimate? This estimate is central for the following budget. How sensitive is the budget on variations of Rmin?
Benthic DIC fluxes are highly sensitive to carbonate dissolution, thus DIC fluxes cannot be used as an estimate for the total mineralization rate. A doubling of R_{min} leads approximately to a two-fold increase of the net A_T generation. This additional information, including a new graph showing the sensitivity of the A_T budget in the SNS towards the choice of R_{min}, was added.

P12419 L3 call this flux fAR = ..
We think it is important to keep the various factors throughout the discussion and in table 5. Thus, we do not use acronyms for any fluxes in these cases. See comment above.

L3 this is a very conservative estimate
We don't understand why this is supposed to be a very conservative estimate.

L7-12 This is a very progressive estimate. You never measured NH4 efflux?
All incubations were sampled also for NH_4^+. NH_4^+ fluxes were calculated and were not significantly different from zero.

L15 on the right hand side 148.4 H2O is generated
This is correct and changed in the manuscript.

L16 It is not "per mole organic matter" but "per carbon atom in organic matter"
This statement is true and the manuscript was revised accordingly.

L25 You use nit=1.51 mmol N m-2 d-1 to calculate denit = nit/0.8 which should result in 1.89 mmol N m-2 d-1. You give the denit rate in C units! Please check whether all following calculations must be revised.
This is true. The denitrification rate is expressed in $mmol\ C\ m^{-2}d^{-1}$ instead of $mmol\ N\ m^{-2}d^{-1}$. Accordingly, the impact of DNF on the A_T budget was recalculated and updated throughout the manuscript.

P12420 L11 eqn (9) should produce 742 H2O
True and corrected in text.

L12 It is not "per mole organic matter" but "per carbon atom in organic matter"
This is correct and changed in the manuscript.

L12-20 In this context the assumption that the amount of iron reduced equals that used for pyrit formation must be explained.
The underlying assumption, that no dissolved iron is escaping the sediment and thus either re-oxidized within the sediments or buried incorporated in solid minerals, is backed up by e.g. Slomp et al. 1997. These authors found generally low fluxes of dissolved iron across the southern North Sea ranging from < 0.05 - 0.25 $mmol\ m^{-2}d^{-1}$, whereas most station display low fluxes < 0.05 $mmol\ m^{-2}d^{-1}$. Manuscript updated.

L21 eqn (10) is rather simplified. Please write a sentence describing the real two-step process.
First, reduced iron reacts with HS^- to form FeS and in a second step the produced FeS reacts with H_2S to form pyrite (FeS_2). Manuscript updated.

P12421 L11 should be Table 5

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Text revised as suggested.

L14 Due to my calculations (new Tab. 5) the percentages are 15%, 19%, 0.4% and 62% which does not sum up to 100% because these relations refer to Rmin = 10 mmol C d-1 m-2.
We do not agree with proposed model and thus we kept the values as submitted. See general comments.

L25 the observed RQ was $\approx$ *1 as claimed on P12413 L22*
The observed RQ was corrected to 0.95 in the text.

P12422 L4 In the following the total budget is presented. Here you should remind the user that this budget refers to the time your observations were taken. The transfer to annual fluxes is problematic.
A note reminding the reader of seasonality of our sampling campaigns was added at the beginning of this section.

L5 eqn (12) should be simplified by using the acronyms I suggested above: Rsed = fCD + fAR ..
We think it is important to keep the different factors throughout the discussion and in table 5. Thus, we do not use acronyms for any fluxes in these cases. See comment above.

L8 My calculations resulted in Rsed=5.88
We do not agree with proposed model. However, due to an error in DNF rate calculation (wrong unit used), this rate is now updated to 6.29 $mmol\ m^{-2}d^{-1}$. See general comments.

P12423 L15 use fCF=5.4 ..
We think it is important to keep the various factors throughout the discussion and in table 5. Thus, we do not use acronyms for any fluxes in these cases. See comment above.

L24 Joint and Pomroy estimated the annual production. Comparing this with summer values is problematic. The value of 199 g C m-2 yr-1 not only includes new but also regenerated production. So your derived daily value is a very high estimate for nitrate fed production. In the end both problems may cancel out. Please discuss this.
Discussion about the seasonality of primary production rates are now added to the manuscript.

P12424 L8 Please use the exact number of 45.45 mmol C m-2 d-1
Text revised as suggested.

L8 should be 36.36 mmol C m-2 d-1
We do not agree with proposed model and thus kept the values like submitted. See general comments.

L14 should be 37.36 mmol C m-2 d-1
We do not agree with proposed model and thus kept the values like submitted. See general comments.

L15 should be 5.99 mmol C m-2 d-1
We do not agree with proposed model and thus kept the values like submitted. See

general comments.

L15 What about pelagic nitrification and the consequences for AT?
Nitrate release by pelagic nitrification is followed by nitrate assimilation by primary production in the water column. Nitrification is included in Eq. 15.

L22 eqn (16) can be written without factors: Rwc = fpp – far ..
We think it is important to keep the different factors throughout the discussion and in table 5. Thus, we do not use acronyms for any fluxes in these cases. See comment above.

L22 Please discuss the possibility of alkalinity advected from the tidal dominated areas (i.e. the Wadden Sea).
Schwichtenberg 2013 estimated that $\approx$ 68 % of the yearly A_T change in the German Bight is due to A_T export from the Wadden Sea. Thomas 2009 estimated an A_T flux from the Wadden Sea into the SNS of 9.6 $mmol\ m^{-2} d^{-1}$. However, as the Wadden Sea is a fully mixed system, any net A_T generation in that area induces an atmospheric CO_2 uptake. Consequently, water masses of the Wadden Sea are in equilibrium with the atmosphere and thus A_T generation in the Wadden Sea plays no role in context of an air-sea CO_2 exchange of the SNS. Considering that, and in absence of reliable Wadden Sea to SNS A_T we decided not to include a flux term for the Wadden Sea. Manuscript updated.

L23 My calculations result in -4.1
We do not agree with proposed model and thus kept the values like submitted. See general comments.

P12425 L3 and L4 Define Vsed and Vwc. A volume? It should rather be a depth integral.
Budget is now expressed as a depth integral.

L5-6 According to my table the values must be corrected.
We do not agree with proposed model and thus kept the values like submitted.

L6 If you recalculate the number of AT generation for the whole SNS give the area you use. I assume that the area with depth < 100 m is larger than 190.411 km2 which is used here.
The annual alkalinity flux for the whole SNS is now calculated using the correct surface area of 329.229 km^2.

L6-8 My calculations resulted in 15% nitrogen cycle and 85% sulfur and iron cycling because I only used primary production, pelagic respiration, benthic aerobic respiration, benthic denitrification and nitrification for the nitrogen cycle. Otherwise one could argue that phosphorus is also involved in all cycles.
Our diagentic models differs from that of the reviewer. As a result, the relative importance of the different elemental cycles for the A_T budget also differ. Furthermore, we indeed consider the P cycle for all diagenetic processes as shown in table 5.

L20-25Pätsch Caution with annual and daily fluxes. and Kühn (2008) also gave numbers for the SNS: 58.6 Gmol N yr-1
We did not use the denitrification rate for the SNS from Paetsch & Kuehn as their SNS is defined differently (enlosing a different surface area) to our SNS and thus might be confusing for the reader.

P12426 L7 here you claim that the pCO2 is governed by the DIC over AT release. DIC release is neglected in the following discussion.
DIC relaese was not neglected in our calculations. The discussion is however strongly revised and clarified, to clarify the role of internal DIC generation in context of changing the pCO_2 of the SNS water.

L11 My calculations resulted in 1.78
We do not agree with proposed model. See general comments. However, due to the update DNF rate, this value was adjusted to 2.33.

L10-15 please give the choice of CO2 constants and the pH scale when using CO2SYS
The calculation was carried out in R using AquaEnv. Manuscript updated.

L21 Direct measurements were taken by Winde et al. 2014 and Moore et al. 2011. Compare their results with your estimates and observations.
Both publications are mentioned now in the introduction chapter.

P12427 L5 -0.7 mmol C m-2 d-1 is only the offset induced by AT generation.
A clarifying comment was added.

L 21 ff. The page numbers at the end of each reference must be cancelled.
The reference list was complied using the official Copernicus bibtex class.

P12437 Are the positions for station 2 and 7 correct?
Yes, the station labeling does not represent the order in which the stations were sam-

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pled.

Add identifiers for the membership in SNS, NNS, SKNT
Table revised as suggested.

P12440 Table 4 is very small. The month of this study in 2012 should be 6
Table revised as suggested.

P12441 Table 5 is very small. Omit b in the eqn for benthic denitrification. Use acronyms for defining the different fluxes. Then you can use them to calculate the budget. "WAR" is pelagic respiration? Say "TA turnover linked to" instead of "Linked to". IR+SR should not be counted for the nitrogen cycle. Omit the P cycle.
We think its important to not just have acronyms, but also the different factors at hand in one table. See general comment. We don't understand why IR+SR should not be counted for the nitrogen cycle, as well as why the P cycle should be omitted. All other suggestions were incorporated in the revised table 5.

P12442 The ticks for lon and lat should match even numbers
Figure changed accordingly.

P12443 There is something wrong with these profiles: Station 11 cannot have a depth of 500 m. In c) there is only one station shown.
Figure 2 (a) represents station 11 with a depth of $\approx$ 30m. Figure 2 (c) shows the profile of station 80. Label corrected.

P12447 Say "scatter plots" instead of "correlation plots". Indeed the reader cannot see any correlation. Please discuss the rank adjustment and the consequences.

Label revised as suggested.

P12449 Fig 8b: The overall regression line is misleading as the slope of the regression lines for each region should result in RQ ≈ 1.
The overall regression line was indeed misleading and is now removed.

Fig8 The auxiliary lines should match the labels at the axes
Grid removed.

P12451 Say "scatter plots" instead of "correlation plots". I do not understand the p value. There is no correlation calculated. Where do the horizontal and vertical bars at some dots come from? In the Figure caption 4 lines are described. In the plot I only see 3. The assignment is not clear.
The p-value describes the correlation between all points displayed in this scatter plot. The dotted/dashed and the long dashed line are almost plotting along the same values and is thus hard to distinguish. Error bars indicate the statistical error of the flux measurements, which were either based on 4 or 5 points. The caption was updated, correlation plots now named scatter plots.

P12452 "Contribution .. to the benthic AT budget .."
Label revised as suggested.

Measured AT flux seems to small in this Fig.
Figure was updated using revised values.

P12453 Where does Fair = 1.3 mmol C m-2 d-1 comes from?. In the text Fair = 0.7

mmol C m-2 d-1
The budget was updated by the new F_{air} flux of 1.0 $mmol\ C\ m^{-2} d^{-1}$. See comments above.

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