

## ***Interactive comment on: "The impact of sedimentary alkalinity release on the water column CO<sub>2</sub> system in the North Sea" by H. Brenner et al.***

H Brenner et al.

*Correspondence to:* H Brenner (heiko.brenner@nioz.nl)

We thank the reviewers for their useful comments and have revised the manuscripts accordingly.

### **Response to reviewer comments by Wei-Jun Cai**

5     *You may want to cite Bauer et al. 2013 in “and between 10 and 25% of the current day oceanic CO<sub>2</sub> 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.*

Reference added.

10

*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 CO<sub>2</sub>, while the low-latitude shelves generally tend to be supersaturated (Chen and Borges, 2009).”*

Reference added.

15

*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 CO<sub>2</sub> was detected using a solid state infra-red CO<sub>2</sub> detector” As far as I know, the sample volume for one analysis is 0.7-1.0 mL.*

20 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  $d[O_2]=dz$  was determined from the gradient in the diffusive boundary layer (Glud, 2008).”*

25 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  
30 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  
35 an entire bay or at a time series observation site*

Text has been revised as suggested: The concentration changes over time of  $O_2$ , DIC and  $A_T$  in the  
overlying water...

*Fig. 4b is not needed. Simply say it is sufficient as there is no correlation for readers to examine.*  
40 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,  
45 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  
50 interface (not necessarily in water column). So it is not necessarily because of water depth*

While this statement is generally true, it has little 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,  
60 explain why we are even expecting the ratio of DIC/O<sub>2</sub> 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.

65 (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.

70 4.4, at the end of discussion aerobic processes (respiration plus  $\text{NH}_4$  oxidation), you should point out the "bottom line" that net TA/DIC (or TA/O<sub>2</sub>) 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: Also note that complete aerobic respiration (i.e. the combination  
75 of aerobic respiration with nitrification consumes 17 mole  $A_T$  per 106 mole of DIC released.

*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 CO<sub>2</sub> not as HCO<sub>3</sub><sup>-</sup> but TNH<sub>4</sub> as NH<sub>4</sub><sup>+</sup> and P as H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (as dominant species). Wouldn't it be easier to use only undissociated form  
80 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.*

85 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.

90

*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/m<sup>2</sup>/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.  
95 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 O<sub>2</sub>, DIC and TA.  
100 No benthic flux or porewater concentration profiles of nutrient, DIC-C13, or Ca<sup>2+</sup>, 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  $A_T$  from the sediment does <NOT> necessarily result in an increase of  $A_T$  whole system, as in the water column, some biogeochemical processes are opposing the  $A_T$  generation in the sediment.”

Text revised as suggested: An efflux of  $A_T$  from the sediment does not necessarily result in an increase of  $A_T$  whole system,...

*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: Based on the analysis above, we can now write an alkalinity balance for the combined sediment and water column of the SNS...

120

4.6, I am glad you said this clearly AT “The direction of a  $CO_2$  flux between the surface water and the atmosphere is determined by the  $pCO_2$  gradient between water and atmosphere, which is ultimately governed by the ratio of internal DIC over internal  $A_T$  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/m<sup>2</sup>/d, and hence, 1.70 mmolC/m<sup>2</sup>/d of  $CO_2$  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  $R_{pp}$  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  $CO_2$  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  $CO_2$  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: A thermocline was formed between 20 - 50 m water depth in all stations  
140 of the NNS and SKNT, but just in two stations of the SNS.

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

145 *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?*  
150 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. There-  
for, 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.

155 *pg 12411 line 8 change colder to cooler and add what it is cooler than.*

Text revised as suggested: As a result, the bottom water in the NNS and SKNT was substantially  
cooler than bottom water in the SNS...

160 *Sentence starting on line 9 make more direct, delete the use of 'hence'.*  
Text revised as suggested: ...one would expect a nearly doubling of the TOU between the NNS and  
SNS due to bottom water temperature, all other environmental factors being the same.

*The paragraph on line 15 would be better served having the discussion of water depth in the para-  
graph before than the discussion of water temp.*  
165 See comment above.

*pg 12417 line 26 The assumption that the overlying water is still always oversaturated with car-  
bonate from research published in 1998 (17 years ago) is probably ok, but with the change in atmo-  
spheric CO2 over the last 17 years makes me question if oversaturation continues year round.*  
170 A more recent study was added as a reference. (Kuhn et al. 2010)

#### **Response to reviewer comments by J. Paetsch**

175 **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.

180

*Very strong assumptions and “gestimates” were made (steady state,  $R_{min}$ ,...). 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.

185 *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 the model output. The rate for DNF was given in the wrong unit and subsequently also the  $A_T$  change was mis-  
190 calculated. 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.

195

*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  $2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ . Similarly the net gener-  
200 ation of DIC amounts to  $1.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ . 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 autochthonous organic matter in both water column and sediment matches the primary production of autochthonous organic matter in the water column). However, as noted above, riverine input of organic matter, and so, respiration of this organic matter releases  $1.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$   
205 of DIC. The internal release of  $2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  of  $A_T$  and  $1.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$  of DIC, will eventually lead to an  $0.96 \text{ mmol m}^{-2} \text{ d}^{-1}$  of  $\text{CO}_2$  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  
210 at all places in the text where this occurs.*

Throughout the manuscript, we tried to compare our June/September values with the best fitting lit-

erature 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.

215

*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  
220 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 CO<sub>2</sub> uptake. We think that the current title suitably covers this story line.

*The unit mmol Eq should be replaced by mmol C*

225 This is now changed throughout the updated manuscript.

***Detailed remarks:***

*P12396 L14 “.. should be considered as an important factor”*

Text revised as suggested: Overall, our results show that sedimentary alkalinity generation should be  
230 considered as an important factor in the...

*L21 Liu et al 2010 never discussed shelf uptake*

Reference removed.

235 *P12397 L8 “.. the question .. which particular drivers ..*

Text revised as suggested: Therefore the question remains which particular drivers are governing the...

*P12399 L4 Pätsch and Kühn 2008 used the 50 m depth contour to separate SNS and NNS. So your  
240 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

245 *L29 “is the only net outflow ..”*

Text revised as suggested: This northwards directed current is the only net outflow of the North Sea and thus...

*P12400 L2 “.. by strong .. currents..”*

250 Text revised as suggested:...the shallow SNS is influenced by strong tidally induced currents and mixing...

*L12 “ .. and near Helgoland in the German Bight (Hebbeln et al., 2003)”*

Text revised as suggested: ...along the Belgian coast, in smaller areas north and east of the German  
255 Bight and near Helgoland in the German Bight...

*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?*

260 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.*

265 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.

270 *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*

275 Station 88 exhibits a median grain size of 21  $\mu m$ . 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  $\mu m$ . Text revised accordingly.

280 *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  $\mu m$  was added in the text and table 1. Column with regions added.

*L19 Which criterion did you use to determine the representativeness?*

285 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. Manuscript updated by a comment pointing that out.

290 *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.

295 *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?*

300 The microprofiling was setup at the most stable (center) part of the ship, to 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.

310 *P12410 L29 “ .. is the bottom temperature exhibiting a north – south gradient in summer, with higher temperatures in the south*

Text revised as suggested" A second important environmental factor controlling the North-South gradient in TOU rates is the bottom temperature exhibiting a north – south gradient in summer,...

315 *P12411 L11 “a nearly doubling ..”*

Text revised as suggested: ...one would expect a nearly doubling of the TOU between the NNS and SNS...

*L14 “.. compared to the SNS (Tab. 3).”*

320 Text revised as suggested: ...lower TOU values recorded compared to the SNS...

*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.

*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: In this expression,  $L$  is the theoretical OPD of the sediment,  $\phi$  is the porosity, and  $D_s$  is the effective diffusivity of  $O_2$  in the pore water (i.e., corrected for tortuosity)  $[O_2]_{bw}$  is the bottom water concentration of  $O_2$  and  $F_{O_2}^0$  is the benthic diffusive oxygen flux. This relationship is based on the balance between diffusive oxygen fluxes and oxygen consumption rates under steady state conditions and negligible advection. The above relation was used to estimate the theoretical

OPD from the measured DOU as shown in Figure...

360

*L24 Fig. 7a does not contain empty circles*

Caption of figure 7 updated.

*L25 Is L the theoretical OPD?*

365 Yes. "Theoretical..." added in the text.

*L26 “ , and [O2]bw is the oxygen concentration in bottom water”*

Yes, manuscript updated.

370 *L26 what is F<sub>0O2</sub> in eqn (3)?*

$F_{O_2}^0$  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.*

375 Reference to figure corrected.

*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.

380

*P12413 L1 The measured OPD is in two cases smaller than the calculated ones. Discuss this. For which stations is this true?*

This is true for station 52 and 65, both stations of the SKNT. Both exceptions are now named in the manuscript.

385

*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.*

390 Equation 3 excludes per definition any other but diffusive transport for DOU rates. See comment above (L 346).

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

Reference to table 2 added..

*L16 Same as for TOU: Fig. 6 should be improved. The dependency of depth and grain size/porosity must be excluded.*

400 Figure 6 shows pairwise correlations between different parameters. For this statistical analysis, it is not required that parameters are independent from each other. See comment above.

*L19 "DIC-flux is correlated with TOU"*

405 Text revised as suggested.

*L20 Fig. 8b is called before 8a. Exchange 8a and 8b.*

Labels for Figure 8 changed. Figure 8a and 8b swapped.

410 *L24 you mean Fig. 8b?*

Now figure 8a.

*P12414 L2 You mean Fig. 8b?*

Figures swapped, now figure 8a

415

*L8 "one mole DIC"*

Text revised as suggested.

*L10 "re-oxidized"*

420 Text revised as suggested.

*L13 "(Fig. 8a)"*

Now figure 8b. Text revised accordingly.

425 *L22 "is in good agreement.."*

Text revised as suggested.

*L23 "The disagreement (e.g.at station 38) .."*

Text revised as suggested.

430

*P12415 L4 mention that these number are mean values.*

Text revised as suggested.

*L12 “(Fig. 8a)”*

435 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<sup>-1</sup> m<sup>-2</sup>*

131.2 Gmol as reported in Thomas et al. (2009) divided by the surface area of the SNS used in that  
440 paper (150392 km<sup>2</sup>) and this divided by 1/4 of the year (365.25/4) indeed yields 9.6 mmol m<sup>-2</sup> d<sup>-1</sup>.  
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<sup>-2</sup> d<sup>-1</sup> alkalinity.

445

*P12416 L16 “assumptions”*

Text revised as suggested.

*P12417 L1 “a high benthic respiration ..”*

450 Text revised as suggested.

*L6-7 “.. invoke the question which processes are generating AT in the sediment”*

Text revised as suggested.

455 *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))*

460 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)*

465 Reference to Paulmier 2009 et al. added.

L26 Give a justification for the estimate  $R_{min} = TOU$ . Why not taking the DIC efflux as estimate?  
This estimate is central for the following budget. How sensitive is the budget on variations of  $R_{min}$ ?  
Benthic DIC fluxes are highly sensitive to carbonate dissolution, thus DIC fluxes cannot be used as  
470 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  $f_{AR} = ..$   
475 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.  
480

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

485 L15 on the right hand side 148.4  $H_2O$  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.  
490

L25 You use  $nit = 1.51 \text{ mmol N m}^{-2} \text{ d}^{-1}$  to calculate  $denit = nit/0.8$  which should result in  $1.89$   
 $\text{mmol N m}^{-2} \text{ d}^{-1}$ . 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  $\text{mmol C m}^{-2} \text{ d}^{-1}$  instead of  $\text{mmol N m}^{-2} \text{ d}^{-1}$ .  
495 Accordingly, the impact of DNF on the  $A_T$  budget was recalculated and updated throughout the  
manuscript.

P12420 L11 eqn (9) should produce 742  $H_2O$   
True and corrected in text.  
500

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 pyrite  
505 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  $< 0.05 - 0.25 \text{ mmol m}^{-2}\text{d}^{-1}$ , whereas most station display low fluxes  $< 0.05$   
510  $\text{mmol m}^{-2}\text{d}^{-1}$ . Manuscript updated.

L21 eqn (10) is rather simplified. Please write a sentence describing the real two-step process.

First, reduced iron reacts with  $\text{HS}^-$  to form  $\text{FeS}$  and in a second step the produced  $\text{FeS}$  reacts with  $\text{H}_2\text{S}$  to form pyrite ( $\text{FeS}_2$ ). Manuscript updated.

515

P12421 L11 should be Table 5

Text revised as suggested.

L14 Due to my calculations (new Tab. 5) the percentages are 15%, 19%, 0.4% and 62% which  
520 does not sum up to 100% because these relations refer to  $R_{\text{min}} = 10 \text{ mmol C d}^{-1} \text{ m}^{-2}$ .

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

525 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  
530 of this section.

L5 eqn (12) should be simplified by using the acronyms I suggested above:  $R_{\text{sed}} = f_{\text{CD}} + f_{\text{AR}}$  ..

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.

535

L8 My calculations resulted in  $R_{\text{sed}}=5.88$

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  $6.29 \text{ mmol m}^{-2}\text{d}^{-1}$ . See general comments.

540 *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.

545 *L24 Joint and Pomroy estimated the annual production. Comparing this with summer values is problematic. The value of  $199 \text{ g C m}^{-2} \text{ yr}^{-1}$  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.

550 *P12424 L8 Please use the exact number of  $45.45 \text{ mmol C m}^{-2} \text{ d}^{-1}$*

Text revised as suggested.

*L8 should be  $36.36 \text{ mmol C m}^{-2} \text{ d}^{-1}$*

We do not agree with proposed model and thus kept the values like submitted. See general comments.

555

*L14 should be  $37.36 \text{ mmol C m}^{-2} \text{ d}^{-1}$*

We do not agree with proposed model and thus kept the values like submitted. See general comments.

*L15 should be  $5.99 \text{ mmol C m}^{-2} \text{ d}^{-1}$*

560 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  $A_T$ ?*

Nitrate release by pelagic nitrification is followed by nitrate assimilation by primary production in the water column. Nitrification is included in Eq. 15.

565

*L22 eqn (16) can be written without factors:  $R_{wc} = f_{pp} - f_{ar}$  ..*

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.

570 *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  $9.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ . 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.

580 *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  $V_{sed}$  and  $V_{wc}$ . A volume? It should rather be a depth integral.*

Budget is now expressed as a depth integral.

585

*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  $A_T$  generation for the whole SNS give the area you use. I assume that the area with depth < 100 m is larger than 190.411 km<sup>2</sup> which is used here.*

590

The annual alkalinity flux for the whole SNS is now calculated using the correct surface area of 329.229 km<sup>2</sup>.

*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.*

595

Our diagenetic 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.

600

*L20-25 Paetsch Caution with annual and daily fluxes. and Kühn (2008) also gave numbers for the SNS: 58.6 Gmol N yr<sup>-1</sup>*

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.

605

*P12426 L7 here you claim that the  $pCO_2$  is governed by the DIC over  $A_T$  release. DIC release is neglected in the following discussion.*

DIC release 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.

610

*L11 My calculations resulted in 1.78*

We do not agree with proposed model. See general comments. However, due to the update DNF rate,  
615 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.

620 *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<sup>-2</sup> d<sup>-1</sup> is only the offset induced by AT generation.*

625 A clarifying comment was added.

*L 21 ff. The page numbers at the end of each reference must be cancelled.*

The reference list was compiled using the official Copernicus bibtex class.

630 *P12437 Are the positions for station 2 and 7 correct?*

Yes, the station labeling does not represent the order in which the stations were sampled.

*Add identifiers for the membership in SNS, NNS, SKNT*

Table revised as suggested.

635 *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.*

640 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  
645 revised table 5.

*P12442 The ticks for lon and lat should match even numbers*

Figure changed accordingly.

650 *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  $\approx 30\text{m}$ . Figure 2 (c) shows the profile of station 80. Label corrected.

655 *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  $RQ \approx 1$ .*

The overall regression line was indeed misleading and is now removed.

*Fig8 The auxiliary lines should match the labels at the axes*

Grid removed.

665

*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.*

670 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 ..”*

675 Label revised as suggested.

*Measured AT flux seems to small in this Fig.*

Figure was updated using revised values.

680 *P12453 Where does  $F_{air} = 1.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$  comes from?. In the text  $F_{air} = 0.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$*

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