Answers to the reviewers of “The impact of intertidal areas on the carbonate system of the southern North Sea” by Fabian Schwichtenberg, Johannes Pätsch, Michael Ernst Böttcher, Helmuth Thomas, Vera Winde, Kay-Christian Emeis.

The authors thank the reviewers for their interest and their detail-rich comments, which helped to improve the manuscript. We followed the suggestions of Referee #1 and re-ordered the methods part. Additionally, we re-organized the discussion section. The former section 4.4. (TA/DIC ratios) was shifted, and has now the numbering 4.2. Following the suggestions of both anonymous referees especially this section has been improved also by including valuable references.

In the following we list all reviewer comments (blue, italic) and give answers (black).

Fabian Große

On a purely technical note, I would suggest that the authors adapt the color palettes they use for their figures. For many of the plots the colors are indistinguishable in greyscale and, thus, for colorblind people. This applies to Figs. 3-5, 8 and 9. Figure 6 lacks a legend.

I am not familiar with ODV color palettes, so I can’t give advice for Figs. 3-5. The other figures seem to be produced with MatLab, for which the authors could either use the ’new’ default color palette parula or any of the cmocean color palettes (https://uk.mathworks.com/matlabcentral/fileexchange/57773-cmoceanperceptually-uniform-colormaps). For Fig. 9, it would suffice to add different markers to the different lines.

We changed the corresponding figures according to the advices. Figures 8 is now black and white, Figure 9 without colors but with different line styles.

Anonymous Referee #1

General comments: This manuscript discusses the role of alkalinity export from the Wadden Sea on the carbonate system of the southern North Sea. Specifically, it aims at quantifying this export, its importance for the alkalinity budget, and the relative role of aerobic versus anaerobic processes in generating the alkalinity in the Wadden Sea.

The manuscript presents interesting work, which is worth publishing, but in my opinion the manuscript itself needs some work. The aim and take home messages of the work are not made very clear in either the abstract or the last paragraph of the introduction. The order and relative length of sections does not always appear logical to me. The construction of the TA budget raises some questions. Also, the manuscript is at times difficult to follow without knowing the details of previous studies, especially in the methods section. For example, the biogeochemistry in the model is merely explained. In short, the writing can be much sharper. In the specific comments I’ll provide examples and suggestions.

Thanks for the detailed review. Within the abstract we added the aims and reorganized the Methods section according to the reviewer's suggestions. The TA budget may have been misleading as the role of "effective river input" was not explained in detail. We added explanations. The biogeochemical model description has been augmented.

Also the presentation of data can be improved. As already indicated in another comment, the figures can be improved to support black & white reading, e.g. by using dashed and dotted lines or bars. I also found the order of the tables highly confusing. If I counted correctly they are presented in the text in the order Table 6 – Table 1 – Table 3 – Table 4 – Table 5 – Table 2. Please change this in the next version.

We improved figures 1, 3, 4, 5, 8, and 9 (old numbering) and changed the order of the tables.

Content-wise, a major point I don't fully understand is the lack of quantification of the uncertainty in the calculated export flux of 39 Gmol TA y-1, which is such a central result of this study. I understand it is based on sparse measurements of DIC and TA concentrations in the different Wadden Sea areas but some estimate of the uncertainty with the use of equation (2) and upscaling of the results should be possible to make.

Within the budgeting section we introduced an estimate of the uncertainty.

Also, using a fixed value for the Wadden Sea export for the years 2001-2009 but taking into account interannual variability in the other terms of the TA budget makes it difficult to actually quantify the relative contributions for each of the years, as you also expect quite some interannual variability in the export flux. I would therefore suggest to also calculate an average TA budget for the period 2001-2009, as you did for the seasonal pattern, and mostly use that in the discussion of the budget. In my opinion, some more odd choices were made in the TA budget, such as excluding Riveff and the leap years, which need revision and/or better explanations.

We added an averaged budget, explained the role of Riveff. The seasonal and annual averages use now all years. We left out all days with date 29 February.

Distinguishing between anaerobic and aerobic processes generating TA in the Wadden Sea appears somewhat problematic, since many processes highly relevant for the TA dynamics are initially not taken into account, but are required to explain your data anyway. Take for example oxidation of methane, but also reoxidation of other reduced species (e.g. previously buried sulphur). Given that there are many different processes, the system is so dynamic and exposure of sediments plays such an important role, how can you be sure that the TA/DIC ratio is a reliable metric for the message you want to convey with respect to aerobic and anaerobic degradation? I also miss a discussion on the relevant time scale of processes here.

This is certainly a valid statement, and processes are in all likelihood comingled. What struck us is the fact that the export ratios are statistically different in the three sectors and that these differences appear to be related to morphological features (areas and strait/channel geometries of the tidal basins) that have previously been invoked to explain differences in eutrophication status. The predominance of organic carbon mineralization by aerobic processes in the North Frisian and of anaerobic processes in West Frisian and Jade Bay is well documented in the observations, even though the data base is limited. The model may be ignorant of these differences, but in our opinion the regional variation in processes is an interesting addition to this manuscript.

The role of the data presented in Table 6 is not entirely clear to me; section 2.7 also does not really seem to match with the rest of the manuscript, especially since in the end they are not used for the TA budget. And if these data have indeed been published elsewhere, it seems unnecessary to publish them here as well.

We use the additional TA and DIC data (now Table 3) in the new ordered section 4.1. and 4.2. as discussion distribution. In total the data were not published elsewhere.

Finally, I do not understand why the model was only validated with 2008 data, whereas there are also data from 2001/2002 (as discussed by the authors) and 2005 available in the CANOBA (or related) datasets. Validating with these data as well, especially with the 2001/2002 data that include multiple seasons, would strengthen the manuscript.

As this study focuses on summer situations in the southern North Sea we added statistics for summer 2001 and 2005 in Table 4 and 5.

Specific comments:

Abstract: I miss a clear aim and a concluding sentence in the abstract. The work is described in lines 23-25, but what is the underlying aim? Confirming the high TA export from the Wadden Sea? Finding out the underlying mechanisms? And similarly, what can we conclude from this work?

We now included the sentence "Aim of this work is to reproduce the observed high summer TA concentrations in the southern North Sea and to differentiate the various sources contributing to these elevated values". Later in the abstract we show that we have reached these aim and give percentages of the different contributors to the elevated Alkalinity concentration in summer. We used the observed TA and DIC concentrations as boundary values for the model. In addition, we used these data for a coarse estimate of the different underlying degradation processes.

L. 18-19: This sentence focuses entirely on the physics of coastal oceans, whereas a major reason for coastal acidification being different from open ocean acidification is the fact that inputs and process rates are much higher. See e.g. Duarte et al (2013) (reference added at the end)

We changed the first sentence of the abstract: "The coastal ocean is strongly affected by ocean acidification because it is shallow, has a low volume, and is in close contact with terrestrial dynamics." In addition, we incorporated the reference Duarte et al (2013) and augmented the corresponding discussion in the introduction.

L. 25: "sources" do you refer to concentrations or fluxes or both here? As the sources are calculated based on measured concentrations and modelled exchange rates, so they are not truly observed.

The basic observation data were DIC and TA concentration. We changed this in the text.

L. 34: can you briefly elaborate what you mean with "weak meteorological blocking conditions"? I'd suggest to paraphrase this in the abstract and explain the term later in the manuscript (e.g. at L. 365 where it appears again).

We followed your suggestions and explained this concept at the end of 3.3.

L. 37-38: does the 'net transport' have a particular direction?

No, it does not have a defined direction. But, normally when westerly winds prevail we have an anti-clockwise circulation like figure 7 August 2008 shows.

L. 38: "internal production" is this the gross or net TA production? Of the water column only, or of the combined water and sediment system?

It is the net TA production including benthic and pelagic processes. "net" is added in the text.

L. 42-43: "anaerobic degradation dominated" with which pathway?

The pathways are denitrification and sulphate- and iron – reduction. We added this in the text.

L. 54-58: Add the suggested mechanisms for the observation in the Provoost article (i.e. change in production-respiration balance). Also refer to Duarte et al (2013) here, as they summarise many important processes impacting pH balance. Now it seems as if only biogeochemical processes in the sediment are important, which is obviously not the case in many coastal areas.

Thanks. Both articles and their arguments are used now.

L. 64-67: Also the Baltic Sea is a key example of this; see e.g. Łukawska-Matuszewska (2017) and Gustafsson et al (2019)

We incorporated these articles and their issues.

L. 87-90: If this is the aim of the work it is not written very clearly. What is the general aim? What is the key research question that will be addressed? Is there a certain time period associated with this or is your aim more general? What do you hypothesise? This section really needs some work.

We changed the text accordingly.

Methods: the division of subsections seems oddly chosen. 11 subsections is way too many and yet details are lacking. Subsection 2.7 seems unnecessary and subsection 2.8 way too short. I would suggest to merge some of the subsections, or use a third level instead.

We followed the reviewers suggestion and introduced a third level. Old section 2.8 was augmented.

L. 158: NO3 data are also presented in this table, but not mentioned here or much discussed in the manuscript.

We use the nitrate data, which are indicated in Table A3 and mentioned this in the text: “Monthly mean concentrations of nitrate, TA and DIC were added for the Dutch rivers (www.waterbase.nl) and for the German river Elbe (Amann et al., 2015).”

L. 178-197: The purpose of this subsection (and of this data in general) is not entirely clear to me and someone it feels like they were added last-minute. Maybe because they are the first presented but referred to as Table 6. Can the authors please elaborate on why this data were added? Especially since in the end they are not used for the calculation of the TA budget. Also, if the data are presented elsewhere (as L. 180-181 seems to suggest, “reported for completeness only”), there is no need to discuss the methodology here.

As already mentioned above the additional TA and DIC data are used in the new ordered section 4.1. and 4.2. as discussion distribution. In total the data were not published elsewhere.

L. 190-197: if this is the novel part of the manuscript, as seems to be suggested by L. 191 (“the main extension in the present study”), then it really needs a more detailed explanation. Also readers not familiar with Pätsch et al. (2018) need to understand this. Explain which biogeochemical processes are involved and where they take place (water column or sediment or both). How are sediments included in general? A brief mention to Wolf-Gladrow et al. (2007) is not sufficient, as I don’t think that the exact same components are included in this study.

The main model extension was indeed the prognostic treatment of TA, which was introduced by Pätsch et al. (2018). We changed this section accordingly and give additional information on pelagic and benthic processes which affect TA variations.

L. 195: “nutrient dynamics” i.e. productivity and decomposition?

We now say: “The pelagic biogeochemical part is driven by planktonic production and respiration, formation and dissolution of calcite, pelagic and benthic degradation and remineralisation, and also by atmospheric deposition of reduced and oxidised nitrogen.”

L. 196: what about atmospheric sulphur deposition?

We use only nitrogen deposition. The model does not treat Sulphur dynamics explicitly.

L. 241-242: I don’t understand why the time lag is the reason for the lack of statistical analysis. The low number of observations is the reason. If this is what you mean, then please paraphrase this section.

We rephrased accordingly: “Due to the low number of concentration measurements a statistical analysis of uncertainties of ΔTA and ΔDIC was not possible.”

L. 257-258: so scenario A has no Wadden Sea export but the same internal biogeochemistry as scenario B? Or is it the same as previously published implementations of the model? Please elaborate.

We rephrased this section and write now: "For scenario B we used the same model configuration as for scenario A and additionally implemented Wadden Sea export rates of TA and DIC as described above."

L. 259-260: So the data in Fig. 2 are calculated according to Eq. 2? And then multiplied by the area of what? Summed area of the grid cells? Please explain.

We sharpened the description of the export rates: "The respective Wadden Sea export rates (Fig. 2) are calculated by the temporal integration of the product of wad_sta and wad_exc over one month."

L. 268-269: This belongs in the introduction. Mention all aims clearly there in the last paragraph.

We mention our aims now in the abstract and in the introduction and omit this sentence at this position.

Results: Sections 3.1. and 3.2: why do you discuss the validation of DIC an TA separately? It seems more logical to me that, because they are so connected, you can also discuss them at the same time. That would also shorten this relatively long section.

We decided to stay with the separation of TA and DIC validation within two separate subchapters as we think that it will be confusing to discuss both parameters together. The structure of both sections is very clear and helps the reader to compare the corresponding features.

L. 303: what do you mean by "the standard deviation improved"? In scenario A it was lower, i.e. 7 umol/kg. Or do you mean to say that the standard deviation comes closer to that of the observations?

We now write: "Compared to scenario A the simulation of scenario B was closer to the observations in terms of RMSE (18 µmol TA kg^{-1}) and the standard deviation (Stdv = 22 µmol TA kg^{-1}). Also the correlation (r = 0.86) improved (Table 4)."

L. 348: rather than mentioning high flushing times, I would paraphrase to focus on the low water renewal or long mean residence time.

We changed this sentence: "They were chosen to highlight the pattern in summer 2003 with one of the highest flushing times (lowest water renewal times), and that in 2008 corresponding to one of the lowest flushing times (highest water renewal times)." In addition, we added the definition of flushing times and the relation to renewal times in section 2.1.2.

Same in L. 351-352: I would paraphrase to say that highest inflows occurred in winter.

We changed this sentence: "Flushing times (rounded to integer values) were consistently higher in summer than in winter, meaning that highest inflow occurred in winter."

L. 354-356: Can't you use a metric to correct for this feature, allowing fairer comparisons?

One of the main statement within our manuscript is that one of the reasons that our annual

Wadden Sea TA export differs from that given by Thomas et al. (2009), is, that the latter authors assumed constant flushing times (6 weeks). We show that for different years and different seasons the flushing times differ strongly. In order to compare the water exchange rate in weeks (Thomas et al., 2009) with our flushing times we stick to this term. We admit that the comparison of flushing times of different basins is not fair, but here we focus on temporal comparisons.

Sections 3.4 and 3.5: Again, I'd suggest to merge these two.

We merged these two sections, stayed with the two-block structure and created an additional common analysis.

L. 385-386: How is this for TA?

As mentioned above, in an additional section we compare both TA and DIC structures.

Discussion: I'd suggest to change the order. Subsection 4.2, which is to a large extent an outlook to the future and partly relies on te TA budget, is much more logical as final subsection.

Subsection 4.5 is connected to the Wadden Sea data and it seems logical for it to immediately follow subsection 4.1.

We followed your suggestions. The order is now:
4.1 Uncertainties
4.2 TA/DIC ratios
4.3 TA budget
4.4 The impact of export

L. 394-396: I don't understand why the model was only validated with 2008 data, whereas there are also data from 2001/2002 (as discussed by the authors) and 2005 available in the CANOBA (or related) datasets. Validating with these data as well, especially with the 2001/2002 data that include multiple seasons, would strengthen the manuscript

We added the statistical validation for summer 2001 and 2005 (Tables 4 and 5)

L. 397-399: Move to last paragraph of introduction, this aim is not in there yet.

We defined our aims in the abstract and in the introduction. We cancelled the listing of these more technical aims in this section.

L. 416-417: This is quite a simplified statement; the temporal and spatial scale you consider are highly relevant for whether this is the case and for which processes associated with anaerobic decomposition this is relevant. See e.g. Hu and Cai (2011) and Gustafsson et al (2019) for discussions on this.

Thanks, we incorporated these sentences: “On longer time scales TA can only be generated by processes that involve permanent loss of anaerobic remineralisation products (Hu and Cai, 2011). A second precondition is the nutrient availability to produce organic matter, which in turn serves as necessary component of anaerobic decomposition (Gustafsson et al., 2019).”

L. 424-428: Could you add some suggestions for improvement?

We added: “More measurements distributed with higher resolution over the annual cycle would clearly improve our estimates.”

L. 431-453: Why is S burial not discussed here? This seems highly relevant, especially on the longer term.

We discuss this now: “Sulphate reduction (not modelled here) also contributes to alkalinity generation. On longer time scales the net effect is vanishing as the major part of the reduced components are immediately re-oxidized in contact with oxygen. Iron- and sulphate -reduction generates TA but only their reaction product iron sulphide (essentially pyrite) conserves the reduced components from re-oxidation. As the formation of pyrite consumes TA, the TA contribution of iron reduction in the North Sea is assumed to be small and to balance that of pyrite formation (Brenner et al., 2016).”

L. 435-437: So external NO3 inputs are not relevant for benthic denitrification?

In our model N_2 production due to denitrification is recharged by OM in relation to the benthic oxygen consumption (Seitzinger and Giblin, 1996). So external nitrate inputs implicitly stimulate this denitrification as the amount of benthic oxygen consumption is stimulated by primary production and the subsequent provision of OM to the benthic realm.

L. 440-441: Why does this compensate the TA generation? Please explain.

We added: “This amount of nitrate would not fully be available for primary production if parts of it would be consumed by denitrification.”

L. 444-446: But how high and relevant is the deposition of these inputs for the TA budget? This is a very qualitative paragraph.

We added: “The average decrease within 6 years is about 0.4 Gmol TA yr^{-1}, whereas the average increase within 3 years is only 0.1 Gmol TA yr^{-1}.”

L. 470-472: So what is the aim of adding these data to the manuscript if they are published elsewhere and not taken into account for the budget?

In total this table is not published elsewhere. In the context of this study it serves supporting the discussion of uncertainties. The data show large variabilities.

L. 478-479: How has the sensitivity of DIC to modelled biology been confirmed?

Figure 8c shows the summer drawdown of DIC which is due to primary production. Also Lorkowski et al., (2012) showed this relation.

L. 479-480: The reader doesn’t know this yet as the TA budget has not yet been presented. I’d suggest to change the order.

Yes, order has been changed.

L. 494-496: Thus slower exchange, what would be the effect on the TA export?

We added: “This would decrease TA export into the North Sea.”

L. 497-499: Why?

We added: “In fine grained silt diffusive transport plays a key role, while in the upper layer of coarse (sandy) sediments advection is the dominant process.”

L. 504-506: On which time scale? Maybe this already occurred in the time period 2001-2009? Could you elaborate on that with the Provoost et al (2010) and Borges and Gypens (2010) papers as references?

We added: “pH values in Dutch coastal waters decreased from 1990 to 2006 drastically. Changes in nutrient variability were identified as possible drivers (Provoost et al., 2010), which is consistent with model simulations by Borges and Gypens (2010).”

L. 527-529: Can you really say that TA variability is more sensitive to Wadden Sea export given that the export is kept constant over the years?. To me it seems you can only make this statement for seasonal variability, not for interannual variability.

*You are right. We induce interannual variability of TA and DIC concentrations mainly by interannual variability of the physical environment. So, we suppose that we underestimate the interannual variability of TA and DIC concentrations. We added “*The interannual variability of the model results are mainly driven by the physical prescribed environment.*”*

L. 534-535: Why is Riveff not taken into account for the budget? Also since you seem to refer to it later in the text (i.e. L. 543-544 “3% were due to river input Riveff of TA”, and L 558, “effective river loads”) If there is a good reason, you need to explain this.

We added: “This is explained in the Method Section “River Input”.” The reason why we introduced “effective river input” is to understand the role of river input on concentration changes.

*L. 541: Why only use non-leap years? You miss two of the nine years in your data set by doing so, and it may create unintentional bias. Also, you can easily correct for it (data/91*90 for the first three months). Again, this is a really odd choice that I don’t understand.*

OK. We recalculated the averages using all years. The data from all 29 of February were cancelled.

L. 544-547: why discussing this if Riveff is not in the budget? Also, referring back to the relevant terms in equation 1 can aid the reader in understanding this statement.

We hope that the concept of $\mathrm{Riv}_{\mathrm{eff}}$ is clear now.

L. 552-556: Where do these percentages come from? If I understand correctly, 47% refers to 14/51 Gmol/t, but this is less than 47%. Similarly for the 59% term, which I assumed was calculated as 17/38 Gmol/t.

You are right, we corrected these percentages. We also added: “Note that these percentages are related to the sum of the absolute values of the budgeting terms.”

L. 557-559: So why are the effective river loads used in this sum and not the actual river loads, which are – apparently – used in the rest of the budget? The construction of the budget and the choices made really need a better explanation.

Here we discuss the sinks and sources, which change the TA concentration necessarily. Net transport and actual river load may change the concentration depending on the concentration of added or leaving water. Please keep in mind that the volume may also change over time due to the free surface elevation. We added: "For the consideration of TA concentration variations we excluded net transport and actual river loads, because these fluxes are diluted and do not necessarily change the TA concentrations."

L. 571-587: What is miss in this paragraph is that there is no discussion of the uncertainty related to differences between the modelled and measured TA concentrations in the North Sea. For example, if you assume that the deviation between measured and modelled TA is entirely due to uncertainties / errors in the Wadden Sea export estimate, what is then the uncertainty in this export?

We added an estimate of the uncertainty of the additional Wadden Sea TA export flux, and added: "Table 4 shows that our scenario B underestimates the observed TA concentration by about 5.1 µmol kg^{-1} in 2008. Scenario A has lower TA concentration than scenario B in the validation area. The difference is about 11 µmol kg^{-1}. This means that the Wadden Sea export of 39 Gmol TA yr^{-1} results in a concentration difference of 11 µmol kg^{-1}. Assuming linearity, the deviation between scenario B and the observations (5.1 µmol kg^{-1}) would be compensated by an additional Wadden Sea export of about 18 Gmol TA yr^{-1}. If we assume that the deviation between observation and scenario B is entirely due to uncertainties or errors in the Wadden Sea export estimate, then the uncertainty of this export is 18 Gmol TA yr^{-1}."

L. 577: "safely" why? Are their characteristics similar enough? Explain.

The Area of the West Frisian Wadden Sea is much larger than the area of the East Frisian Wadden Sea. We changed this sentence: "Due to the scarcity of data, the West Frisian Wadden Sea was not considered in the simulations, but, as the western area is much larger than the eastern area, the amount of exported TA from that area can be assumed to be in the same range as from the East Frisian Wadden Sea (10 to 14 Gmol TA yr^{-1})."

L. 588-606: I assumed that the ECOHAM model also calculates TA generation from the sediments in the German Bight. If not, that should then be better explained in the method section. If yes, what is the magnitude of TA generation in the sediments in the model? How does it compare to the 12.2 Gmol/y estimate of Brenner et al (2016). And can you make a similar upscaling from the result of Burt et al (2016) which was acquired using a different method?

In section 2.1.3 we mention "Benthic denitrification and other anaerobic processes have no impact on pelagic TA concentrations in this model version. Only the carbonate ions from benthic calcite dilution and the remineralisation products ammonium and phosphate which enter the pelagic system across the benthic-pelagic interface alter the pelagic TA concentration."

L. 611-651: My main issue with this section is that many processes highly relevant for the TA dynamics are initially not taken into account, but are required to explain your data anyway. Not only oxidation of methane, but also reoxidation of other reduced species (e.g. previously buried sulphur). You actually run into that problem when discussing your results, noticing you cannot ignore them. So, given that there are many different processes, the system is so dynamic and exposure of sediments plays such an important role, how can you be sure that the TA/DIC ratio is a reliable metric for the message you want to convey with respect to aerobic and anaerobic degradation? I also miss a discussion on the relevant time scale of processes in relation to your results.

Following the suggestions and queries of the two reviewers, we re-organised the entire discussion of the processes relevant to the regional differences in TA/DIC ratios, which is now part of section 4.2. In the course of this re-organisation , we corrected the stoichiometric TA/DIC ratios generated by the putative processes, included relevant references suggested by reviewers, and generally tried to be less assertive with respect to putative sources of TA and DIC.

L. 615-616: I don't think the change in DIC concentration is relevant for the change in TA. TA is reduced during the oxidation of ammonium to nitrate, which consumes acid but doesn't affect the DIC concentration. The impact of aerobic organic matter degradation on TA is minor and only comes from the production of ammonium and phosphate. The changes in DIC obviously impact the TA/DIC ratio, but not the generation or consumption of TA.

We changed the text accordingly, and write now: "Candidate processes are numerous and the export ratios certainly express various combinations, but the most quantitatively relevant likely are aerobic degradation of organic material (resulting in a reduction of TA due to nitrification of ammonia to nitrate with a TA / DIC ratio of -0.16)".

L. 616: The TA/DIC ratio of denitrification is not 1 but 0.8. See e.g. R5 in Table 1 of Rassmann et al (2020).

We changed accordingly and added this reference.

L. 619-620: And what about the sulphur dynamics? E.g. when previously buried reduced sulphur becomes exposed and reoxidised. You need to mention that here already, not only later at L. 624

We added: "Other processes are aerobic (adding only DIC) and anaerobic (TA/DIC ratio of 2) oxidation of upward diffusing methane, oxidation of sedimentary sulphides upon resuspension into an aerated water column (no effect on TA/DIC) followed by oxidation of iron (adding TA), and nitrification of ammonium (consuming TA)."

L. 624: An example of what I wrote above: the ratio becomes negative, but in fact lower than -0.16, so this means that something else besides aerobic decomposition must explain this. You use reoxidation of pyrite, which consumes 2 mol of TA per mol of S oxidised. Besides this *process, also other processes can affect the TA/DIC ratio at the same time. So how can you tell the relative importance of all of them?*

See above

L. 633: Another example: here you need the processes you initially neglected to explain your results.

See above

L. 640-641: How can you know this negative ratio does not result from reoxidation of reduced species?

See above

L. 647-648: Finally a mention of time scales, but please cite Hu and Cai (2011) and/or Gustafsson et al (2019) here.

We added the citation of Hu and Cai (2011): "Taken at face value, the resulting negative ratio of -0.4 implicates re-oxidation of pyrite, normally on timescales of early diagenesis thermodynamically stable (Hu and Cai, 2011), possibly promoted by increasing wind forces and associated aeration and sulphide oxidation of anoxic sediment layers (Kowalski et al., 2013)."

L. 674: The role of allochthonous nitrate is merely discussed in the rest of the manuscript and needs to be elaborated on in the discussion.

We omitted this sentence.

L. 676-689: This "outlook" section is such a large part of the conclusions, but it isn't even a result of your study. I'd suggest to either present it as an "outlook" subsection within your conclusions, or shorten it such that your conclusions actually reflect your manuscript.

We renamed this chapter: "Conclusions and Outlook"

L. 681-684: Why? Explain.

The trend is expected to continue due to the European Water Framework Directive, which requires less nitrogen input. We added: "(European Water Framework Directive)"

L. 713: how was this value estimated? What is the uncertainty and how does this uncertainty impact your budget?

In section 4.1 Uncertainties of .. exchange we added: "We calculated the sensitivity of our annual TA export rates on uncertainties of the Δ-values of Table 1. As the different areas North- and East Frisian Wadden Sea and Jade Bay has different exchange rates of water, for each region the uncertainty of 1 µmol kg^{-1} in ΔTA at all times has been calculated. The East Frisian Wadden Sea export would differ by 0.84 Gmol TA yr^{-1}, the Jade Bay export by 0.09 Gmol TA yr^{-1} and the North Frisian export by 3 Gmol TA yr^{-1}."

L. 756-757: These dates actually fall in autumn and spring, not in winter and summer. Table A3: What is the time span of these data? What is the variation? (s.d. for the mean as well as for the separate months)

Due to the scarcity of the original data, statistic for individual months was not possible. In Table A3 we added SD (standard deviation) of the monthly means. We added in chapter 2.2.2: "The Dutch data were observed in the years 2007 – 2009. The river Elbe data stem from the years 2009 – 2011."

Technical comments:

L. 51: 'regional' is stated twice, please remove the second mentioning

Done

L. 63-64: Ben-Yaakov (1973) also is a seminal paper to mention in this context

We incorporated the reference

L. 75: change "Netherland" to "the Netherlands"

Done

L. 82: it seems that Brenner et al. (2016) and Burt et al. (2016) can also be mentioned here

We incorporated the references

L. 93: The domain of which model? ECOHAM? Should also be clear to readers unfamiliar with Pätsch et al. (2010)

OK, we changed the text accordingly.

L. 97-100: I only understood this when reading the second time. Perhaps rephrase. Also, make clear you use measurements to calculate these box averages.

We changed the text: "For the calculation of box averages of DIC and TA a bias towards the deeper areas with more volume and more data should be avoided. Therefore, each water column covered with data within the validation area delivered one mean value, which is calculated by vertical averaging. These mean water column averages were horizontally interpolated onto the model grid. After this procedure average box values were calculated."

L. 98: "water column" point? grid cell?

It is the water column, because at this stage we have observational data at arbitrary locations.

L. 133: a 1996 reference is used for data from 2001-2009?

Yes, this is the official reference provided by NCEP/NCAR. In addition, we added in the acknowledgements "We used NCEP Reanalysis data provided by the NOAA/OAR/ESRL PSL, Boulder, Colorado, USA, from their Web site at https://psl.noaa.gov/"

L. 144: "below" where exactly?

We introduced this description in the following section.

L. 159: "monthly mean concentrations" also for the years 2001-2009?

We added: "The Dutch river data were observed in the years 2007 – 2009. The river Elbe data were taken in the years 2009 – 2011. These concentration data were prescribed for all simulation years as mean annual cycle.*"*

L. 173-176: please provide units for each of the terms introduced here.

Done

L. 182: add direct link to Pangaea reference.

We now give the DOI

L. 183: volume of Exetainer?

12 ccm

L. 184: volume of bottle?

250 ccm

L. 185: how much HgCl2 added?

100 µl

L. 188: which batch of CRM was used?

It was batch 102. We clarified this in the text.

L. 189: what were the accuracy and precision?

We added: "Standard deviations for DIC and TA measurements were better than +/-2 and +/-10 µmol/kg, respectively."

L. 248: add "the model" to "FVCOM"

Done

L. 251: why not add E1, N1, etc to Fig 1 for clarity, rather than this description?

Done

L. 253: "overall" i.e. cumulative?

The mean daily runoff.

L. 263: "table 4". Also in Table 5, although I would suggest to merge both tables.

The tables were augmented by the years 2001 and 2005. To keep clarity we did not merge the tables.

L. 280: "TA" add "surface-water"

We changed the first sentence of this section: "The results of scenarios A and B were compared with observations of TA in August 2008 (Salt et al., 2013) for surface water."

L. 289: add validation box to Fig 5, possibly also to Figs. 3 and 4.

Done

L. 291: “standard variation” don’t you mean “standard deviation”?

Yes. We changed it in the text.

L. 298: rephrase to “the model underestimated TA”, passive tense seems odd here

Done

L. 299-300: change to “the Dutch Frisian Islands”

Done

L. 369: “TA-concentration” remove hyphen.

Done

L. 395: change to “were also”

Done

L. 460: “this would result in an increased TA concentration of 1 umol/kg”

Done

L. 487: “shift the balance” in which direction / with which result?

This is discussed in the following sentences.

L. 536: “highest variability” in an absolute or a relative sense?

In an absolute sense. We added “absolute”.

L. 554: replace “smaller” by “less”

Done

L. 611-612: add “based on measured concentrations and modelled water fluxes”

We changed in the figure caption for figure 2: “The export rates were calculated for DIC and TA based on measured concentrations and simulated water fluxes.”

L. 614-615: add Brenner et al (2016 as reference)

Done

L. 627: add the TA/DIC ratio of this process (-2).

Following the suggestions and queries of the two reviewers, we re-organised the entire discussion of the processes relevant to the regional differences in TA/DIC ratios, which is now part of section 4.2. In the course of this re-organisation , we corrected the stoichiometric TA/DIC ratios generated by the putative processes, included relevant references suggested by reviewers and generally tried to be less assertive with respect to putative sources of TA and DIC.

L. 645: don’t you mean “organoclastic”?

Thanks, we incorporated this term: ".. and anaerobic processes related to sulphate reduction of organoclastic material (TA / DIC ratio of 1)."

L. 648: add "leading" between "re-oxidised" and "to"

Done

Tables: They are presented in the text in the order Table 6 – Table 1 – Table 3 – Table 4 – Table 5 – Table 2. Please change to a logical order. The aim of Table 6 is not clear.

Done

L. 725: should be "non-leap years"

The exclusion of leap years is cancelled.

L. 728: change "of" to "between"

Done

Table 2: change first header to "Wadden Sea export" for clarity

Done

L. 780: "temporally interpolated"

Done

L. 1172: "values of TA, DIC and NO3"

Done

Table A3: add horizonal lines in between the parameters for clarity.

Done

Figures: As said above, please make them as black & white friendly as possible Fig. 1 (and L. 94): green area is not visible in black & white. Maybe use dashed or dotted lines instead.

We changed the green box into magenta. The dashed line is indicated within the text. This makes the magenta validation box identifiable.

Fig. 6: Add a legend in the figure itself, not only in the caption. Use striped and dotted bars to make black & white friendly

Done. The order of the bars are indicated now.

Fig. 9: What is the purpose of the dots? Also this plot can easily be made black & white friendly.

Done

References - Ben-Yaakov, S., (1973), pH BUFFERING OF PORE WATER OF RECENT ANOXIC MARINE SEDIMENTS, Limnology and Oceanography, 18, doi: 10.4319/lo.1973.18.1.0086. –

Borges, Alberto V., Gypens, Nathalie, (2010), Carbonate chemistry in the coastal zone responds more strongly to eutrophication than ocean acidification, Limnology and Oceanography, 55, doi: 10.4319/lo.2010.55.1.0346. –

Duarte, C.M., Hendriks, I.E., Moore, T.S. et al. Is Ocean Acidification an Open- Ocean Syndrome? Understanding Anthropogenic Impacts on Seawater pH. Estuaries and Coasts 36, 221–236 (2013). https://doi.org/10.1007/s12237-013-9594-3 -

Hu, X., and Cai, W.-J. (2011), An assessment of ocean margin anaerobic processes on oceanic alkalinity budget, Global Biogeochem. Cycles, 25, GB3003, doi:10.1029/2010GB003859. –

Gustafsson, Erik; Hagens, Mathilde; Sun, Xiaole; Reed, Daniel C.; Humborg, Christoph; Slomp, Caroline P.; Gustafsson, Bo G. (2019) Sedimentary alkalinity generation and long-term alkalinity development in the Baltic Sea. Biogeosciences, 16, 437-456, doi:10.5194/bg-16-437-2019. –

Łukawska- Matuszewska, K. and Graca, B.: Pore water alkalinity below the permanent halocline in the Gdánsk Deep (Baltic Sea) – Concentration variability and benthic fluxes, Marine Chemistry, 204,49–61, https://doi.org/10.1016/j.marchem.2018.05.011, 2018 –

Rassmann, J., Eitel, E. M., Lansard, B., Cathalot, C., Brandily, C., Taillefert, M., Rabouille, C., (2020) Benthic alkalinity and dissolved inorganic carbon fluxes in the Rhône River prodelta generated by decoupled aerobic and anaerobic processes. Biogeosciences, 17, 13-33, doi:10.5194/bg-17-13-2020.

Anonymous Referee #2

The authors examined the impacts of alkalinity export from the Wadden Sea tidal flats on the carbonate system in the southern North Sea, mainly using a digital modeling method. The topic is interesting, and the result explanation looks fair. However, I find one of their references (Pätsch et al., 2018) had demonstrated the same issue using similar or even the same digital model. So the novelty should be further refined. Also it is difficult for me to follow the manuscript, due to the poor organization of the text and the insufficient annotation of charts.

We thank the reviewer for the interest and the helpful review. Pätsch et al. (2018) used indeed a similar model. Only the benthic module has been exchanged. The novelty of the study in hand is the scientific question: Which TA contributors cause the elevated TA concentration elevations in the southern North Sea and German Bight during summer? How large are the different fluxes? These aims are now clearly defined in the abstract and in a broader manner within the introduction. Reviewer#1 also found need of improvement of the general structure. We reorganized the Methods and Discussion chapter. Also, the annotation of charts has been improved.

Major concerns

1. The study area is unclearly defined. As an Asian reader, Figure 1 is quite unfriendly for me. For example, where are "the German Bight as well as parts of the Danish and the Dutch coast" (lines 94-95)? Also the Wadden Sea is strange for me. After a internet searching, I know that the Wadden Sea is the largest tidal flats system in the world (https://www.waddensea-worldheritage.org/). Since the Wadden Sea is a key area in this study, its geography should be clearly introduced to readers. I suggest that a striking section or subsection of "Study area" should be set up, after the Introduction. In this section or subsection, more geographical details and biogeochemical knowledge should be presented. Some contents of the currect subsections 2.6.1 and 2.9.1 could be integrated in the subsection of Study area.

We added a map into Figure 1, where all these areas are identified. We augmented the third section of the introduction where the area of the Wadden Sea was described. We added: "During low tide about 50 % of the area are falling dry (van Beusekom et al., 2019). Large rivers discharge nutrients into the Wadden Sea, which in turn shows a high degree of eutrophication, aggravated by mineralisation of organic material imported into the Wadden Sea from the open North Sea (van Beusekom et al., 2012)."

2. The model structure and settings are unclear. A structure diagram is needed. As for the the submodule HAMSOM and the original ECOHAM model, some details are needed here, although their "details were described by Backhaus & Hainbucher (1987) and Pohlmann (1996)" (lines 107-109). At least their background and assumptions and fundamental structure and application strengths and limitations should be introduced. I wonder whether it is specially designed for the area under study. This information is also critical for general *readers. In the current subsection 2.8, the authors said that "The main extension in the present study was the introduction of a prognostic treatment of TA (Pätsch et al., 2018)" (Lines 191-192). I wonder whether they give any modification on Pätsch et al. (2018) treatment.*

We added a structure diagram as supplemental material. For HAMSOM we added: "It is a baroclinic primitive equation model using the hydrostatic and Boussinesq approximation. It is applied to several regional sea areas worldwide.". For this study we use the ECOHAM version of Pätsch et al. (2018). Only the benthic module is exchanged. We added: "The pelagic biogeochemical part is driven by planktonic production and respiration, formation and dissolution of calcite, pelagic and benthic degradation and remineralisation, and also by atmospheric deposition of reduced and oxidised nitrogen. All these processes impact TA. Benthic denitrification and other anaerobic processes have no impact on pelagic TA concentrations in this model version. Only the carbonate ions from benthic calcite dilution and the remineralisation products ammonium and phosphate which enter the pelagic system across the benthic-pelagic interface alter the pelagic TA concentration.".

3. How did the authors plot Figure 2? There is no relevant information (such as data source) in both the figure caption and main text. Since Figure 2 is the key to distinguish the two scenarios defined in this study, this information is a must to be clarified

In the new chapter "2.3 The Wadden Sea" the data behind Fig. 2 are described in detail. In chapter 2.1.3. we added: "The respective Wadden Sea export rates (Fig. 2) are calculated by the temporal integration of the product of wad_sta and wad_exc over one month (see equation 2)." In the figure caption we have now: "Figure 2: Monthly Wadden Sea export of DIC and TA [Gmol mon^{-1}] at the North Frisian coast (N), East Frisian coast (E) and the Jade Bay in scenario B. The export rates were calculated for DIC and TA based on measured concentrations and simulated water fluxes.".

Some minor comments and suggestions

1. To avoid confusion, please unify abbreviations for North Frisian coast (N or NF),East Frisian coast (E or EF) and Jade bay (J or JB).

Done

"The respective areas 1-3" in line 350 also refers to the three regions?

The three areas concerning the flushing times are the validation area and the western and eastern part of the validation area. We added in chapter "3.3 Hydrodynamic conditions and flushing times": "The flushing times were determined for the three areas 1 – validation area, 2 – western part of the validation area, 3 – eastern part of the validation area.". In addition we define in chapter "2.1.1 Model domain and validation area": ".The validation area is divided by the magenta dashed line at 7° E into the western and eastern part.".

2. What is "yr" in Equation (1)? Please clarify.

yr = year. We clarified this in the text.

3. Lines 440-441: Why does this partly compensate the missing TA generation by benthic denitrification? Please explain.

We added: ". This amount of nitrate would not fully be available for primary production if parts of it would be consumed by denitrification.".

4. Line 453: Carbonate dissolution cannot be counteracted by DIC additions. DIC additions (mostly refer to free CO2) are usually in favor of carbonate dissolution.

We rephrased this section: "Dissolution Dissolution of biogenic carbonates may be an efficient additional enhancement of the CO_2 buffer capacity (that is: source of TA), since most of the tidal flat surface sediments contain carbonate shell debris (Hild, 1997). On the other hand, shallow oxidation of biogenic methane formed in deep and shallow tidal flat sediments (not modelled) (Höpner & Michaelis, 1994; Neira & Rackemann, 1996; Böttcher et al., 2007) has the potential to lower the buffer capacity, thus counteracting or balancing the respective effect of carbonate dissolution."

5. Lines 534-535: Why was Riv_eff not taken into account for the budget calculations? I notice that the authors mentioned it to the later discussion, i.e. lines 557-559 "Summing up the source and sinks, Wadeen Sea exchange rates, internal processes and effective river loads resulted in highest sums in 2002 and 2003 and lowest in 2009".

This was also an issue of Reviewer#1. We clarified this point in chapter "2.2.2 River input": "Bulk alkalinity discharged by rivers is quite large but most of the rivers entering the North Sea (here the German Bight) have lower TA concentrations than the sea water. In case of identical concentrations the effective river load Riv_{eff} is zero. The TA related molecules enter the sea, and in most cases they are leaving it via transport. In case of tracing or budgeting both the real TA river discharge and the transport must be recognized. In order to understand TA concentration changes in the sea Riv_{eff} is appropriate.".

6. Line 552-556: How to get those percentages (47%, 10% and 59%) based on results

in Table 2. Please clarify.

This was also an issue of Reviewer#1. We added in chapter "4.3 TA budgets and variability of TA mass in the German Bight": "Comparing the absolute values of all sources and sinks of the mean year results in a relative ranking of the processes.". The values has been changed, as in the previous version we erroneously excluded the actual river input.

7. Lines 615-616: The reduction of TA here is associated with the oxidation of ammonium to nitrate, instead of the change in DIC. Refers to Zhai et al. (2017,

https://doi.org/10.1016/j.ecss.2017.08.027).

We changed the text: ".. and nitrification of ammonium (consuming TA, TA/DIC ratio is -2, see Pätsch et al., 2018 and Zhai et al., 2017).".

8. Lines 617-619: The TA/DIC ratio of denitrification is not 1 but 0.8.

We changed : " denitrification (TA / DIC ratio of 0.8, see Rassmann et al., 2020)"

The TA/DIC ratio of sulphate reduction is not 2 but 1. Refers to Sippo et al. (2016), Are mangroves drivers or buffers of coastal acidification? Insights from alkalinity and dissolved inorganic carbon export estimates across a latitudinal transect, Global Biogeochemical Cycles, 30, 753–766, doi:10.1002/2015GB005324.

We added: ".. and anaerobic processes related to sulphate reduction of organoclastic material (TA / DIC ratio of 1, see Sippo et al., 2016)."

9. Lines 619-620: The authors mentioned that aerobic and anaerobic oxidation of upward diffusing methane were not considered in present study. How to relate this statement to line 633 "When sulphate reduction associated with organic matter and/or methane oxidation and pyrite burial became the dominant processes..."?

We cancelled the content of lines 619-620

10. Lines 624-638 and Figure 9: TA/DIC ratios of <–0.16 in regions under study may indicate other processes than aerobic decomposition (–0.16) and anaerobic reaction (>0). What are them? I would like to suggest the authors mention more possible processes at the beginning of Section 4.4.

We added: "Candidate processes are numerous and the export ratios certainly express various combinations, but the most quantitatively relevant likely are aerobic degradation of organic material (resulting in a reduction of TA due to nitrification of ammonia to nitrate with a TA / DIC ratio of -0.16), denitrification (TA / DIC ratio of 0.8, see Rassmann et al., 2020), and anaerobic processes related to sulphate reduction of organoclastic material (TA / DIC ratio of 1, see Sippo et al., 2016). Other processes are aerobic (adding only DIC) and anaerobic (TA/DIC ratio of 2) oxidation of upward diffusing methane, oxidation of sedimentary sulphides upon resuspension into an aerated water column (no effect on TA/DIC) followed by oxidation of iron (adding TA), and nitrification of ammonium (consuming TA)."

11. Table 2 is discussed after all other tables. Please change the order of the tables. Additionally, Table 6 can be shifted to the Appendix.

Done

12. Are those TA/DIC ratios presented in Figure 9 mean values in the given regions? Please clarify.

The basis of Fig. 9 are the data of the new Table 1. This means that the TA/DIC ratios are not average values. We added a corresponding statement in the caption of Fig. 9.

Also I would like to suggest the authors compare all data in grid cells with the typical stoichiometric ratios of biogeochemical processes. Refers to Figure 4 in Sippo et al. (2016), Global Biogeochemical Cycles.

Fig. 4 in Sippo et al. (2016) shows measured data. Our new Table 1 comprises too less data for such an exercise. To use simulated data is not necessary, as the different processes (if included in the model) are known.

13. The "Wadden Sea tidal flats" should appear in the title.

As we only analysed parts of the Wadden Sea we stay with the old title.

The impact of intertidal areas on the carbonate system of the southern North Sea

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Abstract

The coastal ocean is strongly affected by ocean acidification because it is shallow ~~and~~, has a low volume, and is in close contact with terrestrial dynamics. Earlier observations of dissolved inorganic carbon (DIC) and total alkalinity (TA) in the southern part of the North Sea and the German Bight, a Northwest-European shelf sea, have revealed lower acidification effects than expected. It has been assumed that anaerobic degradation and subsequent TA release in the adjacent back-barrier tidal areas (‘Wadden Sea’) in summer time is responsible for this phenomenon. In this study the exchange rates of TA and DIC between the Wadden Sea tidal basins and the North Sea and the consequences for the carbonate system in the German Bight are estimated using a 3-D ecosystem model. Aim of this work is to reproduce the observed high summer TA concentrations in the southern North Sea and to differentiate the various sources contributing to these elevated values.

Observed TA and DIC ~~sources~~ concentrations in the Wadden Sea ~~were~~are considered as model boundary conditions. This procedure ~~is based on~~acknowledges the dynamic behaviour of the Wadden Sea as an area of effective production and decomposition of organic material. In addition, modelled tidal water mass exchange ~~was~~is used to transport material between the open North Sea and the Wadden Sea. In the model, 39 Gmol TA yr^{-1} were exported from the Wadden Sea into the North Sea, which is lower than a previous estimate, but within a comparable range. Furthermore, the interannual variabilities of TA and DIC concentrations, which were mainly driven by hydrodynamic conditions, were examined for the years 2001 – 2009. Variability in the carbonate system of the German Bight is related to weather in that the occurrence of weak meteorological “blocking situations” leads to enhanced accumulation of TA there. The results suggest that the Wadden Sea is an important driver of the carbonate system variability in the southern North Sea. According to the model results, on average ~~63~~41 % of all TA mass changes in the German Bight ~~were~~are caused by river input, 37 % by net transport~~, 25~~ from adjacent North Sea sectors, 16 % by Wadden Sea export, ~~9 % were~~6 % are caused by the internal net production of TA~~ and 3 % caused by effective~~. The effect on TA ~~river loads (i.e.~~concentration change are very low for river ~~load including~~input, as these freshwater ~~dilution).~~fluxes on average slightly dilute the marine TA concentration. The ratio of exported TA and DIC reflects the dominant underlying biogeochemical processes in the different Wadden Sea areas. Aerobic degradation of organic matter plays a key role in the North Frisian Wadden Sea during all seasons of the year. In the East Frisian Wadden Sea anaerobic degradation of organic matter dominated, including denitrification, sulphate, and iron reduction.

1. Introduction

Shelf seas are highly productive areas constituting the interface between the inhabited coastal areas and the global ocean. Although they represent only 7.6% of the world ocean’s area, current estimates assume that they contribute approximately 21% ~~of~~to total global ocean CO$_2$ sequestration (Borges, 2011). At the global scale the uncertainties of these estimates are significant due to the lack of spatially and temporally resolved field data. Some studies investigated regional carbon cycles in ~~regional~~ detail (e.g., Kempe & Pegler, 1991; Brasse et al., 1999; Reimer et al., 1999; Thomas et al., 2004; 2009; Artioli et al., 2012;

Lorkowski et al., 2012; Burt et al., 2016; Shadwick et al., 2011; Laruelle et al., 2014; Carvalho et al., 2017) and pointed out sources of uncertainties specifically for coastal settings. ~~For example~~ pH variations in coastal- and shelf regions, for example, can be up to an order of magnitude higher than in the open ocean (Provoost et al, 2010). ~~The~~Also, the nearshore effects of CO_2 uptake and acidification are difficult to determine, because of the shallow water depth and a possible superposition by benthic-pelagic coupling~~. Strong~~, and strong variations in fluxes of TA are associated with inflow of nutrients from rivers, pelagic nutrient driven production and respiration (Provoost et al., 2010), submarine groundwater discharge (SGD~~)~~; Winde et al., 2014), and from benthic-pelagic pore water exchange (e.g., Billerbeck et al., 2006; Riedel et al., 2010; Moore et al., 2011; Winde et al., 2014; Santos et al., 2012; 2015; Brenner et al., 2016; Burt et al., 2014, 2016; Seibert et al., 2019). Finally, shifts within the carbonate system are driven by impacts from watershed processes and amplified by changes in ecosystem structure and metabolism (Duarte et al., 2013).

Berner et al. (1970) and Ben-Yakoov (1973) were ~~one of~~among the first who investigated elevated TA ~~in anoxic pore water sediments~~and pH variations caused by microbial dissimilatory sulphate reduction~~. Further studies were conducted, for instance, at~~ in the anoxic pore water of sediments. At the Californian coast~~ (Dollar et al., 1991; Smith & Hollibaugh, 1993; Chambers et al., 1994). There~~, the observed enhanced TA export from sediments was related to the burial of reduced sulphur compounds (pyrite) (Dollar et al., 1991; Smith & Hollibaugh, 1993; Chambers et al., 1994).~~).~~ Other studies conducted in the Satilla and Altamaha estuaries and the adjacent continental shelf found non-conservative mixing lines of TA versus salinity, which was attributed to anaerobic TA production in nearshore sediments (Wang & Cai, 2004; Cai et al., 2010). Iron dynamics and pyrite formation in the Baltic Sea were found to impact benthic TA generation from the sediments (Gustafsson et al., 2019; Łukawska-Matuszewska and Graca, 2017).

The focus of the present study is the southern part of the North Sea located on the Northwest European Shelf. This shallow part of the North Sea is connected with the tidal ~~areas~~basins of the Wadden Sea via deep channels between barrier islands enabling an exchange of water, and dissolved and suspended material (Rullkötter, 2009; Lettmann et al., 2009; Kohlmeier and Ebenhöh, 2009). The Wadden Sea extends from Den Helder (~~Netherland~~The Netherlands) in the west to Esbjerg (Denmark) in the north ~~covering~~and covers an area of about 9500 km^2 (Ehlers, 1994). The entire system is characterised by semidiurnal tides with a tidal range between 1.5 m in the ~~most westerly~~westernmost part and 4 m in the estuaries of the rivers Weser and Elbe (Streif, 1990). During low tide about 50 % of the area are falling dry (van Beusekom et al., 2019). Large rivers discharge nutrients into the Wadden Sea, which in turn shows a high degree of eutrophication, aggravated by mineralisation of organic material imported into the Wadden Sea from the open North Sea (van Beusekom et al., 2012).

In comparison to the central and northern part of the North Sea, TA concentrations in the southern part are significantly elevated during summer (Salt et al., 2013; Thomas et al., 2009~~).~~; Brenner et al., 2016; Burt et al., 2016). The observed high TA concentrations have been attributed to an impact from the adjacent tidal areas (Hoppema, 1990; Kempe & Pegler, 1991; Brasse et al., 1999; Reimer et al., 1999; Thomas et al., 2009; Winde et al., 2014~~).~~), but this impact has not been rigorously quantified. Using several assumptions, Thomas et al. (2009) calculated an annual TA export from the Wadden Sea / Southern Bight of 73 Gmol TA yr^{-1} to close the TA budget for the entire North Sea.

~~Additional data~~The aim of this study is to reproduce the elevated summer concentrations of TA in the southern North Sea with a 3D biogeochemical model that has TA as prognostic variable. With this tool in hand, we budget TA in the relevant area on an annual basis. Quantifying the different budget terms, like river input, ~~of anaerobic TA production in the~~ Wadden Sea ~~and nitrogen deposition in combination with a 3-D model system permit us to~~ export, internal pelagic and benthic production, degradation and respiration allows to determine the most important contributors to TA variations. In this way we refine the budget terms by Thomas et al. (2009) and replace the original closing term ~~with~~by data. The new results are discussed on the background of the ~~budgeting assumptions of~~budget approach proposed by Thomas et al. (2009).

2. Methods

2.1. Model specifications

~~2.1.~~2.1.1. *Model domain and validation area*

The ECOHAM model domain for this study (Fig. 1) was first applied by Pätsch et al. (2010). For model validations (~~green~~magenta: validation area, Fig. 1), an area was chosen that includes the German Bight as well as parts of the Danish and the Dutch coast. The western boundary of the validation area is situated at 4.5° E. The southern and northern boundaries are at 53.5° and 55.5° N, respectively. The validation area is divided by the magenta dashed line at 7° E into the western and eastern part. For the calculation of box averages of DIC and TA a bias towards the deeper areas with more volume and more data should be avoided. Therefore, each water column ~~(having~~covered with data~~)~~ within the validation area delivered one mean value, which is calculated by ~~volume-weighted~~ vertical averaging. ~~In the case of sparse observational data, which cluster towards the coast, these~~These mean water column averages were horizontally interpolated onto the model grid. After this procedure~~,~~ ~~area-weighted~~ average box values were calculated. In case of box-averaging model output, the same procedure was applied, but without horizontal interpolation.

~~2.2.~~2.1.2. The hydrodynamic module

The physical parameters temperature, salinity, horizontal and vertical advection as well as turbulent mixing were calculated by the submodule HAMSOM (Backhaus, 1985), which was integrated in the ECOHAM model. It is a baroclinic primitive equation model using the hydrostatic and Boussinesq approximation. It is applied to several regional sea areas worldwide. Details are described by Backhaus & Hainbucher (1987) and Pohlmann (1996). The hydrodynamic model ran prior to the biogeochemical part. Daily result fields were stored for driving the biogeochemical model in offline mode. Surface elevation, temperature and salinity resulting from the Northwest European Shelf model application (Lorkowski et al., 2012) were used as boundary conditions at the southern and northern boundaries. The temperature of the shelf run by Lorkowski et al. (2012) showed a constant offset compared with observations (their Fig. 3), because incoming solar radiation was calculated too high. For the present simulations the shelf run has been repeated with adequate solar radiation forcing.

River-induced horizontal transport due to the hydraulic gradient is incorporated (Große et al., 2017; Kerimoglu et al., 2018). This component of the hydrodynamic horizontal transport corresponds to the amount of freshwater discharge.

Within this study we use the term flushing time. It is the average time when a basin is filled with lateral advected water. The flushing time is depending on the specific basin. Large basins have usually higher flushing times than smaller basins. High flushing times correspond with low water renewal times.

2.1.3. The biogeochemical module

The relevant biogeochemical processes and their parameterisations have been detailed in Lorkowski et al. (2012). In former model setups TA was restored to prescribed values derived from observations (Thomas et al., 2009) with a relaxation time of two weeks (Kühn et al., 2010; Lorkowski et al., 2012). The changes in TA treatment for the study at hand is described below. Results from the Northwest European Shelf model application (Lorkowski et al., 2012) were used as boundary conditions for the recent biogeochemical simulations at the southern and northern boundaries (Fig. 1).

The main model extension was the introduction of a prognostic treatment of TA in order to study the impact of biogeochemical and physical driven changes of TA onto the carbonate system and especially on acidification (Pätsch et al., 2018). The physical part contains advective and mixing processes as well as dilution by riverine freshwater input. The pelagic biogeochemical part is driven by planktonic production and respiration, formation and dissolution of calcite, pelagic and benthic degradation and remineralisation, and also by atmospheric deposition of reduced and oxidised nitrogen. All these processes impact TA. Benthic denitrification and other anaerobic processes have no impact on pelagic TA concentrations in this model version. Only the carbonate ions from benthic calcite dilution and the remineralisation products ammonium and phosphate which enter the pelagic system across the benthic-pelagic interface alter the pelagic TA concentration. The theoretical background to this has been outlined by Wolf-Gladrow et al. (2007).

The years 2001 to 2009 were simulated with 3 spin up years in 2000. Two different scenarios (A and B) were conducted. Scenario A is the reference scenario without implementation of any Wadden Sea processes. For scenario B we used the same model configuration as for scenario A and additionally implemented Wadden Sea export rates of TA and DIC as described above. The respective Wadden Sea export rates (Fig. 2) are calculated by the temporal integration of the product of wad sta and wad exc over one month (see equation 2).

2.2. External sources and boundary conditions

~~2.3.~~2.2.1. *Freshwater discharge*

Daily data of freshwater fluxes from 16 rivers were used (Fig. 1). For the German Bight and the other continental rivers daily observations of runoff provided by Pätsch & Lenhart (2008) were incorporated. The discharges of the rivers Elbe, Weser and Ems were increased by 21%, 19% and 30% in order to take additional drainage into account that originated from the area downstream of the respective points of observation (Radach and Pätsch, 2007). The respective tracer loads were increased accordingly. The data of Neal (2002) were implemented for the British rivers for all years with daily values for freshwater. The annual amounts of freshwater of the different rivers are shown in the appendix (Table A1). Riverine freshwater discharge was also considered for the calculation of the concentrations of all biogeochemical tracers in the model.

~~2.4.1.1.1. *Meteorological forcing*~~

~~The meteorological forcing was provided by NCEP Reanalysis (Kalnay et al., 1996) and interpolated on the model grid field. It consisted of six-hourly fields of air temperature, relative humidity, cloud coverage, wind speed, atmospheric pressure, and wind stress for every year. 2-hourly and daily mean short wave radiation were calculated from astronomic insolation and cloudiness with an improved formula (Lorkowski et al., 2012).~~

~~2.5.1.1.1. *The biogeochemical module*~~

~~The relevant biogeochemical processes and their parameterisations have been detailed in Lorkowski et al. (2012). In former model setups TA was restored to prescribed values derived from observations (Thomas et al., 2009) with a relaxation time of two weeks (Kühn et al., 2010; Lorkowski et al., 2012). The changes in TA treatment for the study at hand is described below. Results from the Northwest European Shelf model application (Lorkowski et al., 2012) were used as boundary conditions for the recent biogeochemical simulations at the southern and northern boundaries (Fig. 1).~~

~~2.6.~~2.2.2. *River input*

~~2.6.1.~~ Data sources

River load data for the main continental rivers were taken from the report by Pätsch & Lenhart (2008) that was kept up to date continuously so that data for the years 2007 – 2009 were also available (https://wiki.cen.uni-hamburg.de/ifm/ECOHAM/DATA_RIVER). They calculated daily loads of nutrients and organic matter based on data provided by the different river authorities. Additionally, loads of the River Eider were calculated according to Johannsen et al. (2008).

Up to now, all ECOHAM applications used constant riverine DIC concentrations. TA was not used. For the study at hand we introduced time varying riverine TA and DIC concentrations. New data of freshwater discharge were introduced, as well as TA and DIC loads for the British rivers (Neal, 2002). Monthly mean concentrations of nitrate, TA and DIC were added for the Dutch rivers (www.waterbase.nl) and for the German river Elbe (Amann et al., 2015). The Dutch river data were observed in the years 2007 – 2009. The river Elbe data were taken in the years 2009 – 2011. These concentration data were prescribed for all simulation years as mean annual cycle.

The data sources and positions of the river mouths of all 16 rivers are shown in Table A2 and in Fig. 1. The respective riverine concentrations of TA and DIC are given in Table A3. The Dutch data were observed in the years 2007 – 2009. The river Elbe data stem from the years 2009 – 2011. Schwichtenberg (2013) describes the river data in detail.

A few small flood gates (“Siel”) and rivers transport fresh water from the recharge areas into the intertidal areas (Streif, 1990). The recharge areas for these inlets differ considerably from each other, leading to different relative contributions for the fresh water input. Whereas the catchments of Schweiburger Siel (22.2 km^2) and the Hooksieler Binnentief are only of minor importance, the Vareler Siel, the Eckenwarder Siel, and the Maade Siel are of medium importance, and the highest contribution may originate from the Wangersiel, the Dangaster Siel, and the Jade-Wapeler Siel (Lipinski, 1999).

~~2.6.2.~~ Effective river input

In order to analyse the net effect of river input, the effective river input (*Riv*$_{eff}$~~)~~ [Gmol yr^{-1}]) is introduced:

$$Riv_{eff} = \cancel{\frac{\Delta C|_{riv}}{yr}} \frac{\Delta C|_{riv}}{\rho \cdot yr} \cdot V \cdot C \qquad (1)$$

with $\Delta C|_{riv}$ [µmol kg^{-1}] : the concentration change in the river mouth cell due to river load *riv* and the freshwater flux from the river. *V* [l] is the volume of the river mouth cell~~.~~, ρ [kg l^{-1}] density of water, yr is one year, C [10^{-15} l^{-1}] is a constant.

~~*2.7. Sampling of DIC and TA*~~

~~DIC and TA concentrations for selected freshwater inlets sampled in October 2010 and May 2011 are presented in Table 6.~~Bulk alkalinity discharged by rivers is quite large but most of the rivers entering the North Sea (here the German Bight) have lower TA concentrations than the sea water. In case of identical concentrations the effective river load Riv_{eff} is zero. The TA related molecules enter the sea, and in most cases they are leaving it via transport. In case of tracing or budgeting both the real TA river discharge and the transport must be recognized. In order to understand TA concentration changes in the sea Riv_{eff} is appropriate.

2.2.3. Meteorological forcing

The meteorological forcing was provided by NCEP Reanalysis (Kalnay et al., 1996) and interpolated on the model grid field. It consisted of six-hourly fields of air temperature, relative humidity, cloud coverage, wind speed, atmospheric pressure, and wind stress for every year. 2-hourly and daily mean short wave radiation were calculated from astronomic insolation and cloudiness with an improved formula (Lorkowski et al., 2012).

2.3. The Wadden Sea

~~Sampling and analyses took place as described by Winde et al. (2014) and are here reported for completeness only. The data are deposited in the data base https://www.pangaea.de. The samples for TA measurements were filled without headspace into pre-cleaned Exetainer®, filled with 0.1ml saturated $HgCl_2$ solution. The samples for DIC analysis were completely filled into ground-glass-stoppered bottles, and then poisoned with saturated $HgCl_2$ solution. The DIC concentrations were determined at IOW by coulometric titration according to Johnson et al. (1993), using reference material provided by A. Dickson (University of California, San Diego; Dickson et al., 2003) for the calibration. TA was measured by potentiometric titration using HCl using a Schott titri plus equipped with an IOline electrode A157.~~

~~*2.8. Concept of Alkalinity and the carbonate system*~~

~~The main extension in the present study was the introduction of a prognostic treatment of TA (Pätsch et al., 2018) in order to study the impact of biogeochemical and physical changes of TA onto the carbonate system and especially on acidification. The physical part contained advective and mixing processes as well as dilution by riverine freshwater input. The biogeochemical part was driven by formation and dissolution of calcite, nutrient dynamics and also by atmospheric deposition of reduced and oxidised nitrogen. The theoretical background to this has been outlined by Wolf-Gladrow et al. (2007).~~

~~*2.9.*~~*2.3.1. Implementation of Wadden Sea dynamics*

For the present study the exchange of TA and DIC between North Sea and Wadden Sea was implemented into the model by defining sinks and sources of TA and DIC for some of the south-eastern cells of the North Sea grid (Fig. 1). The cells with adjacent Wadden Sea were separated into three exchange areas: The East Frisian~~ and~~, the North Frisian Wadden Sea ~~as well as~~and the Jade Bay, ~~distinguished~~marked by “E”, “N” and “J” (Fig. 1, right side).

Two parameters were determined in order to quantify the TA and DIC exchange between the Wadden Sea and the North Sea.

1. Concentration changes of pelagic TA and DIC in the Wadden Sea during one tide, and
2. Water mass exchange between the back-barrier islands and the open sea during one tide

Measured concentrations of TA and DIC (Winde, 2013; Winde et al., 2014) as well as modelled water mass exchange rates of the export areas by Grashorn (2015) served as ~~basis~~bases for the calculated exchange. Details on flux calculations and measurements are described below. The daily Wadden Sea exchange of TA and DIC was calculated as:

$$wad\_flu = \frac{wad\_sta * wad\_exc}{vol} \qquad (2)$$

Differences in measured concentrations in the Wadden Sea during rising and falling water levels were temporally interpolated and summarized as *wad_sta* [mmol m^{-3}]. Modelled daily Wadden Sea exchange rates of water masses (tidal prisms during falling water level) were defined as *wad_exc* [m^3 d^{-1}], and the volume of the corresponding North Sea grid cell was *vol* [m^3]. *wad_flu* [mmol m^{-3} d^{-1}] were the daily concentration changes of TA and DIC in the respective North Sea grid cells.

In fact, some amounts of the tidal prisms return without mixing with North Sea water, and calculations of Wadden Sea – North Sea exchange should therefore consider flushing times in the respective back-barrier areas. Since differences in measured concentrations between rising and falling water levels were used, this effect is already assumed to be represented in the data. This approach enabled the use of tidal prisms without consideration of any flushing times.

~~2.9.1.~~2.3.2. Wadden Sea - measurements

The flux calculations for the Wadden Sea – North Sea exchange were carried out ~~representatively~~ in tidal basins of the East and North Frisian Wadden Sea (Spiekeroog Island, Sylt-Rømø) as well as in the Jade Bay. For the present study seawater samples ~~were used on~~representing tidal cycles during different seasons (Winde, 2013). The mean concentrations of TA and DIC during rising and falling water levels and the respective differences (ΔTA and ΔDIC) are given in Table 1. Measurements in August 2002 were taken from Moore et al. (2011). The Δ-values were used as *wad_sta* and were linearly interpolated between the times of observations for the simulations. ~~Of course~~In this procedure, the linear progress of the Δ-values ~~did~~does not represent the natural behaviour perfectly, especially if only few data are available. As a consequence, possible short events of high TA and DIC export rates that occurred in periods outside the observation periods may have been missed.

~~A~~Due to the low number of concentration measurements a statistical analysis of uncertainties of ΔTA and ΔDIC was not possible~~, because concentrations~~. They were measured with a lag of 2 hours after low tide and high tide. This was done in order to obtain representative concentrations of rising and falling water levels. As a consequence, only 2 - 3 measurements for each location and season were considered for calculations of ΔTA and ΔDIC.

~~2.9.2.~~2.3.3. Wadden Sea – modelling the exchange rates

Grashorn (2015) performed the hydrodynamic computations of exchanged water masses (*wad_exc*) with the model FVCOM (Chen et al., 2003) by adding up the cumulative seaward transport during falling water level (tidal prisms) between the back-barrier islands that were located near the respective ECOHAM cells with adjacent Wadden Sea area. These values are given in Table ~~3~~2 for each ECOHAM cell in the respective export areas. The definition of the first cell N1 and the last cell E4 is in accordance to the clockwise order in Fig. 1 (right side). The ~~overall~~mean daily runoff of all N-, J- and E-positions was 8.1 km³ d^{-1}, 0.8 km³ d^{-1} and 2.3 km³d^{-1} respectively.

~~*2.10. Model Setup*~~

2.3.4. Additional Sampling of DIC and TA

DIC and TA concentrations for selected freshwater inlets sampled in October 2010 and May 2011 are presented in Table 3. Sampling and analyses took place as described by Winde et al. (2014) and are here reported for completeness and input for discussion only. The autumn data are deposited under doi:10.1594/PANGEA.841976. The samples for TA measurements were filled without headspace into pre-cleaned 12 ccm Exetainer®, filled with 0.1ml saturated $HgCl_2$ solution. The samples for DIC analysis were completely filled into 250 ccm ground-glass-stoppered bottles, and then poisoned with 100 µl of a saturated $HgCl_2$ solution. The DIC concentrations were determined at IOW by coulometric titration according to Johnson et al. (1993), using reference material provided by A. Dickson (University of California, San Diego; Dickson et al., 2003) for the calibration (batch 102). TA was measured by potentiometric titration using HCl using a Schott titri plus equipped with an IOline electrode A157. Standard deviations for DIC and TA measurements were better than +/-2 and +/-10 µmol kg^{-1}, respectively.

~~The years 2001 to 2009 were simulated with 3 spin up years in 2000. Two different scenarios (A and B) were conducted. Scenario A is the reference scenario without implementation of any Wadden Sea processes. Wadden Sea export rates of TA and DIC were implemented in the second scenario (B) as described above. The respective Wadden Sea export rates are shown in Fig. 2.~~

~~2.11.~~2.4. *Statistical analysis*

A statistical overview of the simulation results in comparison to the observations (Salt et al., 2013) is given in Table 4 and 5. In the validation area (~~green~~magenta box in Fig. 1) observations of 10 different stations were available, each with four to six measurements at different depths (51 measured points). Measured TA and DIC concentrations of each point were compared with modelled TA and DIC concentrations in the respective grid cells, respectively. The standard deviations (Stdv), the root mean square errors (RMSE), and correlation coefficients (r) were calculated for each simulation. ~~One aim of this model development was to reduce the RMSE in order to bring the simulated TA concentrations closer to observations.~~In addition to the year 2008, which we focus on in this study, observations were performed at the same positions in summer 2005 and 2001. These data are also statistically compared with the model results.

3. Results

3.1. Model validation - TA concentrations in summer 2008

The results of scenarios A and B were compared with observations of TA in August 2008 (Salt et al., 2013~~).~~) for surface water. The observations revealed high TA concentrations in the German Bight (east of 7°E and south of 55°N) and around the Danish coast (around 56°N) as shown in Fig. 3a. The observed concentrations in these areas ranged between 2350 and 2387 µmol TA kg^{-1}. These findings were in accordance with observed TA concentrations in August / September 2001 (Thomas et al., 2009). TA concentrations in other parts of the ~~observed~~observation domain ranged between 2270 µmol TA kg^{-1} near the British coast (53°N – 56°N) and 2330 µmol TA kg^{-1} near the Dutch coast and the Channel. In the validation box the overall average and the standard deviation of all observed TA concentrations (Stdv) was 2334 and 33 µmol TA kg^{-1}, respectively.

In scenario A the simulated surface TA concentrations showed a more homogeneous pattern than observations with maximum values of 2396 µmol TA kg^{-1} at the western part of the Dutch coast and even higher (2450 µmol TA kg^{-1}) in the river mouth of the Wash estuary at the British coast. Minimum values of 2235 and 2274 µmol TA kg^{-1} were simulated at the mouths of the rivers Elbe and Firth of Forth. The modelled TA concentration ranged from 2332 to 2351 µmol TA kg^{-1} in the German Bight and in the Jade Bay. Strongest underestimations in relation to observations are located in a band close to the coast stretching from the East Frisian Islands to 57° N at the Danish coast (Fig. ~~5a~~4a). The deviation of simulation results of scenario A from observations in the validation box was represented by a RMSE of 28 µmol TA kg^{-1}. The standard ~~variation~~deviation was 7 µmol TA kg^{-1} and the correlation amounted to r=0.77 (Table 4). In the years 2005 and 2001 similar statistical values are found, but the correlation coefficient was smaller.

The scenario B was based on a Wadden Sea export of TA and DIC as described above. The major difference in TA concentrations of this scenario compared to A occurred east of 6.5°E. ~~There surface~~Surface TA concentrations there peaked in the Jade Bay (2769 µmol TA kg^{-1}) and were elevated off the North Frisian and Danish coasts from 54.2° to 56° N (> 2400 µmol TA kg^{-1}). Strongest ~~overestimations~~underestimations in relation to observations ~~appear~~are noted off the Danish coast between 56 and 57° N (Fig. ~~5b~~4b). In the German Bight the model overestimated the observations ~~were~~ slightly ~~overestimated~~, while at the East ~~Frisan~~Frisian Islands the model ~~overestimates~~underestimates TA. When approaching the ~~Netherland's~~Dutch Frisian Islands the simulation ~~underestimates~~overestimates TA compared to observations~~. Near~~ and strongest overestimations can be seen near the river mouth of River Rhine ~~stronger overestimations can be seen.~~. Compared to scenario A ~~it was possible to bring~~ the simulation of scenario B was closer to the observations ~~(~~in terms of RMSE~~=~~ (18 µmol TA kg^{-1}~~). Also~~) and the standard deviation (Stdv = 22 µmol TA kg^{-1}~~) and~~). Also the correlation (r = 0.86) improved (Table 4). In the years 2001 and 2005 the observed mean values are slightly overestimated by the model. The statistical values for 2001 are better than for 2005, where scenario A better compares with the observations.

3.2. Model validation - DIC concentrations in summer 2008

Analogously to TA the ~~simulations~~simulation results were compared with surface observations of DIC concentrations in summer 2008 (Salt et al., 2013). They also revealed high values in the German Bight (east of 7 °E and south of 55°N) and around the Danish coast (near 56°N) which is shown in Fig. ~~4~~5. The observed DIC concentrations in these areas ranged between 2110 and 2173 µmol DIC kg^{-1}. Observed DIC concentrations in other parts of the model domain ranged between 2030 and 2070 µmol DIC kg^{-1} in the north western part and 2080 - 2117 µmol DIC kg^{-1} at the Dutch coast. In the validation box the overall average and the standard deviation of all observed DIC concentrations were 2108 and 25.09 µmol DIC kg^{-1}, respectively.

The DIC concentrations in scenario A ranged between 1935 and 1977 µmol DIC kg^{-1} at the North Frisian~~-~~ and Danish ~~coasts~~coast (54.5°N - 55.5°N) and 1965 µmol DIC kg^{-1} in the Jade Bay. Maxima of up to 2164 µmol DIC kg^{-1} were modelled at the western part of the Dutch coast north of the mouth of River Rhine (Fig. ~~4~~5). The DIC concentrations in the German Bight showed a heterogeneous pattern in the model, and sometimes values decreased from west to east, which ~~is in contradiction to~~contrasts the observations (Fig. ~~4a~~5a). This may be the reason for the negative correlation coefficient r= -0.64 between model and observations (Table 5). The significant deviation from observation of results from scenario A is also indicated by the RMSE of 43 µmol DIC kg^{-1}, and a standard deviation of 14 µmol DIC kg^{-1}. In 2001 and 2005 the simulation results of this scenario A are better, which is expressed in positive correlation coefficients and small RMSE values.

In scenario B the surface DIC concentrations at the Wadden Sea coasts increased: The North Frisian coast shows concentrations of up to 2200 µmol ~~DICkg~~DIC kg^{-1} while the German Bight has values of 2100 – 2160 µmol DIC kg^{-1}, and~~ the~~ Jade Bay concentrations were higher than 2250 µmol DIC kg^{-1}. The other areas are comparable to scenario A. In scenario B the RMSE in the validation box decreased to 26 µmol DIC kg^{-1} in comparison to scenario A. The standard deviation decreased to 9.1 µmol DIC kg^{-1}, and the correlation improved ~~and was r=0.55 (Table 5).~~to r=0.55 (Table 5). The average values are close to the observed ones for all years, even though in 2005 a large RMSE was found.

The comparison between observations and simulation results of scenario A (Fig. ~~5a~~4c) clearly show model underestimations in the south-eastern area~~,~~ and are strongest in the inner German Bight towards the North Frisian coast (> 120 µmol DIC kg^{-1}). Scenario B ~~still produces too low~~also models values lower than observations in the south-eastern area (Fig. ~~5b~~4d), but the agreement between observation and model results is reasonable. Only off the Danish coast near 6.5°E, 56° N the model ~~understimates~~underestimates DIC by 93 µmol DIC kg^{-1}.

3.3. Hydrodynamic conditions and flushing times

The calculations of Wadden Sea TA export in Thomas et al. (2009) were based on several assumptions concerning riverine input of bulk TA and nitrate, atmospheric deposition of

NOx, water column inventories of nitrate and the exchange between the Southern Bight and the adjacent North Sea (Lenhart et al., 1995). The latter was computed by considering that the water in the Southern Bight is flushed with water of the adjacent open North Sea at time scales of six weeks. For the study at hand, flushing times in the validation area in summer and winter are presented for the years 2001 to 2009 in Fig. 6. Additionally, monthly mean flow patterns of the model area are presented for June, July and August for the years 2003 and 2008, respectively (Fig. 7). They were chosen to highlight the pattern in summer 2003 with one of the highest flushing times~~,~~ (lowest water renewal times), and that in 2008 corresponding to one of the lowest flushing times~~.~~ (highest water renewal times).

~~The flushing times~~The flushing times were determined for the three areas 1 – validation area, 2 – western part of the validation area, 3 – eastern part of the validation area. They were calculated by dividing the total volume of the respective areas 1 – 3 by the total inflow into the areas $m^3 (m^3 s^{-1})^{-1}$. Flushing times (rounded to integer values) were consistently higher in summer than in winter~~. Summer values~~, meaning that highest inflow occurred in winter. Summer flushing times in the whole validation area ranged from 54 days in 2008 to 81 days in 2003 and 2006, whereas the winter values in the same area ranged from 32 days in 2008 to 51 days in 2003 and 2009. The flushing times in the western and eastern part of the validation area were smaller due to the smaller box sizes. Due to the position, flushing times in the western part were consistently shorter than in the eastern part. These differences ranged from 5 days in winter 2002 to 14 days in summer 2006 and 2008. The interannual variabilities of all areas were higher in summer than in winter.

The North Sea is mainly characterised by an anti-clockwise circulation pattern (Otto et al., 1990; Pätsch et al., 2017). This can be observed for the summer months in 2008 (Fig. 7). More disturbed circulation patterns in the south-eastern part of the model domain occurred in June 2003: In the German Bight and in the adjacent western area two gyres with reversed rotating direction are dominant. In August 2003 the complete eastern part shows a clockwise rotation which is due to ~~a~~the effect of easterly winds as opposed to prevalent westerlies. In this context such a situation is called meteorological blocking situation.

3.4. Seasonal and interannual variability of TA and DIC concentrations

The ~~years~~period from 2001 to 2009 ~~were~~was simulated for the scenarios A and B. For both scenarios monthly mean surface concentrations of TA were calculated in the validation area and are shown in Fig. 8a and 8b. The highest TA~~-~~ concentration in scenario A was 2329 µmol TA kg^{-1} and occurred in July 2003. The lowest TA concentrations in each year were about 2313 to 2318 µmol TA kg^{-1} and occurred in February and March. Scenario B showed generally higher values: Summer concentrations were in the range of 2348 to 2362 µmol TA kg^{-1} and the values peaked in 2003. The lowest values occurred in the years 2004 – 2008. Also winter values were higher in scenario B than in scenario A: They range from 2322 to 2335 µmol TA kg^{-1}.

~~3.5. Seasonal and interannual variability of DIC concentrations~~

~~Along the lines of~~Corresponding to TA, monthly mean surface DIC concentrations in the validation area are shown in Fig. 8c and 8d. In scenario A the concentrations increased from October to February and decreased from March to August (Fig. 8c). In scenario B the time interval with increasing concentrations was extended into March. Maximum values of 2152 to 2172 µmol DIC kg^{-1} in scenario A occur in February and March of each model year, and minimum values of 2060 to 2080 µmol DIC kg^{-1} in August. Scenario B shows generally higher values: Highest values in February and March are 2161 to 2191 µmol DIC kg^{-1}. Lowest values in August range from 2095 to 2112 µmol DIC kg^{-1}. The amplitude of the annual cycle is smaller in scenario B, because the Wadden Sea export shows highest values in summer (Fig. 2).

The pattern of the monthly TA and DIC concentrations of the reference scenario A differ drastically in that TA does not show a strong seasonal variability, whereas DIC does vary significantly. In case of DIC this is due to the biological drawdown during summer. On the other hand the additional input (scenario B) from the Wadden Sea in summer creates a strong seasonality for TA and instead flattens the variations in DIC.

4. Discussion

~~The aim of this study is to mechanistically test the estimates of~~ Thomas et al. (2009) ~~on~~estimated the ~~contributions~~contribution of shallow intertidal and subtidal areas to the alkalinity budget of the SE North Sea. That estimate (by closure of mass fluxes) was about 73 Gmol TA yr^{-1} originating from the Wadden Sea fringing the southern and eastern coast. These calculations were based on observations from the CANOBA dataset in 2001 and 2002. The observed high TA concentrations in the south eastern North Sea were also ~~were~~ encountered in August 2008 (Salt et al., 2013) and these measurements were used for the main model validation in this study. Our simulations result in 39 Gmol TA yr^{-1} as export from the Wadden Sea into the North Sea. ~~A second aim is to differentiate between and quantify the individual sources.~~ Former modelling studies of the carbonate system of the North Sea (Artioli et al., 2012, Lorkowski et al., 2012) did not consider the Wadden Sea as a source of TA and DIC~~. They showed~~, and good to reasonable agreement to observations from the CANOBA dataset was only achieved in ~~large parts of~~ the open North Sea in 2001 / 2002 (Thomas et al., 2009). Subsequent simulations that included TA export from aerobic and anaerobic processes in the sediment improved the agreement between data and models (Pätsch et al., 2018). When focusing on the German Bight, however, the observed high TA concentrations in summer measurements east of 7°E could not be simulated satisfactorily.

The present study confirms the Wadden Sea as an important TA source for the German Bight and quantifies the annual Wadden Sea TA export rate to 39 Gmol TA yr^{-1}. Additionally, the contributions by most important rivers have been more precisely quantified and narrow down uncertainties in the budgets of TA and DIC in the German Bight. All steps that were required to calculate the budget including uncertainties are discussed in the following.

4.1. Uncertainties of Wadden Sea – German Bight exchange rates of TA and DIC

The Wadden Sea is an area of effective benthic decomposition of organic material (Böttcher et al., 2004; Billerbeck et al., 2006; Al-Rai et al., 2009; van Beusekom et al., 2012) originating both from land and from the North Sea (Thomas et al., 2009). ~~Anaerobic~~In general, anaerobic decomposition of the organic matter generates TA and increases the CO_2 buffer capacity of seawater. On longer time scales TA can only be generated by processes that involve permanent loss of anaerobic remineralisation products (Hu and Cai, 2011). A second precondition is the nutrient availability to produce organic matter, which in turn serves as necessary component of anaerobic decomposition (Gustafsson et al., 2019). The Wadden Sea export rates of TA and DIC modelled in the present study are based on concentration measurements during tidal cycles in the years 2002 and 2009 to 2011 (Table 1), and on calculated tidal prisms of two day-periods that are considered to be representative of annual mean values. This approach introduces uncertainties with respect to the true amplitudes of concentrations differences in the tidal cycle and in seasonality due to the fact that differences in concentrations during falling and rising water levels were linearly interpolated. These interpolated values are based on four to five measurements in the three export areas and were conducted in different years. Consequently, the approach does not reproduce the exact TA and DIC concentrations in the years 2001 to 2009, because only meteorological forcing, river loads and nitrogen deposition were specified for these particular years. The simulation of scenario B thus only approximates Wadden Sea export rates. More measurements distributed with higher resolution over the annual cycle would clearly improve our estimates. Nevertheless, the implementation of Wadden Sea export rates ~~resulted~~here results in improved reproduction of observed high TA concentrations in the German Bight in summer in comparison to the reference run A (Fig. 3).

We calculated the sensitivity of our modelled annual TA export rates on uncertainties of the Δ-values of Table 1. As the different areas North- and East Frisian Wadden Sea and Jade Bay has different exchange rates of water, for each region the uncertainty of 1 µmol kg^{-1} in ΔTA at all times has been calculated. The East Frisian Wadden Sea export would differ by 0.84 Gmol TA yr^{-1}, the Jade Bay export by 0.09 Gmol TA yr^{-1} and the North Frisian export by 3 Gmol TA yr^{-1}.

Primary processes that contribute to the TA generation in the Wadden Sea are denitrification, sulphate reduction, or processes that are coupled to sulphate reduction and other processes (Thomas et al., 2009). In our model, the implemented benthic denitrification does not generate TA (Seitzinger & Giblin, 1996), because modelled benthic denitrification does not consume nitrate (Pätsch & Kühn, 2008). Benthic denitrification is coupled to nitrification in the upper layer of the sediment (Raaphorst et al., 1990), giving reason for neglecting TA generation by this process in the model. The modelled production of N_2 by benthic denitrification falls in the range of 20 – 25 Gmol N yr^{-1} in the validation area, which would result in a TA production of about 19 – 23 Gmol TA yr^{-1} (Brenner et al., 2016). In the model nitrate uptake by phytoplankton ~~is in the range of~~produces about 40 Gmol TA yr^{-1}, which partly compensates the missing TA generation by benthic denitrification. This amount of nitrate would not fully be available for primary production if parts of it would be consumed by denitrification. Different from this, the TA budget of Thomas et al. (2009) included estimates for the entire benthic denitrification as a TA generating process.

Sulphate reduction (not modelled here) also contributes to alkalinity generation. On longer time scales the net effect is vanishing as the major part of the reduced components are immediately re-oxidized in contact with oxygen. Iron- and sulphate - reduction generates TA but only their reaction product iron sulphide (essentially pyrite) conserves the reduced components from re-oxidation. As the formation of pyrite consumes TA, the TA contribution of iron reduction in the North Sea is assumed to be small and to balance that of pyrite formation (Brenner et al., 2016).

Atmospheric nitrogen deposition is taken into account in the simulations. Oxidised N-species (NO_x) dominate reduced species (NH_y) slightly in the validation area during 6 out of 9 simulation years. This implies that the deposition of dissolved inorganic nitrogen decreases TA in 6 of 9 years. The average decrease within 6 years is about 0.4 Gmol TA yr^{-1}, whereas the average increase within 3 years is only 0.1 Gmol TA yr^{-1}. Thomas et al. (2009) also assumed a dominance of oxidised species and consequently defined a negative contribution to the TA budget.

Dissolution of biogenic carbonates may be an efficient additional enhancement of the CO_2 buffer capacity (that is: source of TA~~,~~), since most of the tidal flat surface sediments contain carbonate shell debris (Hild, 1997). On the other hand, shallow oxidation of biogenic methane formed in deep and shallow tidal flat sediments (not modelled) (Höpner & Michaelis, 1994; Neira & Rackemann, 1996; Böttcher et al., ~~2007) is a source of DIC that counteracts carbonate dissolution.~~2007) has the potential to lower the buffer capacity, thus counteracting or balancing the respective effect of carbonate dissolution. The impact of methane oxidation on the developing TA/DIC ratio in surface sediments, however, is complex and controlled by a number of superimposing biogeochemical processes (e.g., Akam et al., 2020).

The net effect of evaporation and precipitation in the Wadden Sea also has to be considered in budgeting TA. Although these processes are balanced in the North Sea (Schott, 1966), enhanced evaporation can occur in the Wadden Sea due to increased heating during low tide around noon. Onken & Riethmüller (2010) estimated an annual negative freshwater budget in the Hörnum Basin based on long-term hydrographic time series from observations in a tidal channel. From this data a mean salinity difference between flood and ebb currents of approximately -0.02 is calculated. This would result in an ~~increasing~~increased TA concentration ~~by~~of 1 µmol TA kg^{-1}, which is the range of the inaccuracy of measurements. Furthermore, the enhanced evaporation estimated from subtle salinity changes interferes with potential input of submarine groundwater into the ~~Wadden Sea, as has~~tidal basins, that been identified by Moore et al. (2011~~) and~~), Winde et al. (2014), and Santos et al. (2015). The magnitude of this input is difficult to estimate at present, for example from salinity differences between flood and ebb tides, because the composition of SGD passing the sediment-water interfacial mixing zone has to be known. Although first characteristics have been reported (Moore et al., 2011; Winde et al., 2014; Santos et al., 2015), the quantitative effect of additional DIC, TA, and nutrient input via both fresh and recirculated SGD into the Wadden Sea remains unclear.

An input of potential significance are small inlets that provide fresh water as well as DIC and TA (Table ~~6~~3). The current data base for seasonal dynamics of this source, however, is ~~patchy~~limited and, therefore, this source cannot yet be considered quantitatively in budgeting approaches.

4 ~~The impact~~TA / DIC ratios over the course of the year

Ratios of TA and DIC generated in the tidal basins (Table 1) give some indication of the dominant biogeochemical mineralisation and re-oxidation processes occurring in the sediments of individual Wadden Sea sectors, although these processes have not been explicitly modelled here (Chen & Wang, 1999; Zeebe & Wolf-Gladrow, 2001; Thomas et al. 2009; Sippo et al., 2016; Wurgaft et al., 2019; Akam et al., 2020). Candidate processes are numerous and the export ratios certainly express various combinations, but the most quantitatively relevant likely are aerobic degradation of organic material (resulting in a reduction of TA due to nitrification of ammonia to nitrate with a TA / DIC ratio of -0.16), denitrification (TA / DIC ratio of 0.8, see Rassmann et al., 2020), and anaerobic processes related to sulphate reduction of organoclastic material (TA / DIC ratio of 1, see Sippo et al., 2016). Other processes are aerobic (adding only DIC) and anaerobic (TA/DIC ratio of 2) oxidation of upward diffusing methane, oxidation of sedimentary sulphides upon resuspension into an aerated water column (no effect on TA/DIC) followed by oxidation of iron (adding TA), and nitrification of ammonium (consuming TA, TA/DIC ratio is -2, see Pätsch et al., 2018 and Zhai et al. 2017).

The TA/DIC export ratios of DIC and TA for the individual tidal basins in three Wadden Sea sectors (East Frisian, Jade Bay and North Frisian) as calculated from observed ΔTA and ΔDIC over tidal cycles in different seasons are depicted in Fig. 9. They may give an indication of regionally and seasonally varying processes occurring in the sediments of the three study regions. The ratios vary between 0.2 and 0.5 in the North Frisian Wadden Sea with slightly more TA than DIC generated in spring, summer and autumn, and winter having a negative ratio of -0.5. The winter ratio coincides with very small measured differences of DIC in imported and exported ~~TA and DIC on the~~ waters (ΔDIC = -2 µmol kg^{-1}) and the negative TA/DIC ratio may thus be spurious. The range of ratios in the other seasons is consistent with sulphate reduction and denitrification as the dominant processes in the North Frisian tidal basins.

The TA / DIC ratios in the Jade Bay samples were consistently higher than those in the North Frisian tidal basin and vary between 1 and 2 in spring and summer, suggesting a significant contribution by organoclastic sulphate reduction and anaerobic oxidation of methane (Al-Raei et al., 2009). The negative ratio of -0.4 in autumn is difficult to explain with remineralisation or re-oxidation processes, but as with the fall ratio in Frisian tidal basin, it coincides with a small change in ΔDIC (-3 µmol kg^{-1}) at positive ΔTA (8 µmol kg^{-1}). Taken at face value, the resulting negative ratio of -0.4 implicates a re-oxidation of pyrite, normally on timescales of early diagenesis thermodynamically stable (Hu and Cai, 2011), possibly promoted by increasing wind forces and associated aeration and sulphide oxidation of anoxic sediment layers (Kowalski et al., 2013). The DIC export rate from Jade Bay had its minimum in autumn, consistent with a limited supply and mineralisation of organic matter, possibly modified by seasonally changing impacts from small tidal inlets (Table 3).

The TA / DIC ratio of the East Frisian Wadden Sea is in the approximate range of those in Jade Bay, but has one unusually high ratio in November caused by a significant increase in TA of 14 µmol kg^{-1} at a low increase of 5 µmol kg^{-1} in DIC. Barring an analytical artefact, the maximum ratio of 3 may reflect a short-term effect of iron reduction.

Based on these results, processes in the North Frisian Wadden Sea export area differ from the East Frisian Wadden Sea and the Jade Bay areas. The DIC export rates suggest that significant amounts of organic matter were degraded in North Frisian tidal basins, possibly controlled by higher daily exchanged water masses in the North Frisian (8.1 km^3 d^{-1}) than in the East Frisian Wadden Sea (2.3 km^3 d^{-1}) and in the Jade Bay (0.8 km^3 d^{-1}) (compare Table 2). On the other hand, TA export rates of the North Frisian and the East Frisian Wadden Sea were in the same range.

~~***4.2.***~~ Regional differences in organic matter mineralisation in the Wadden Sea have been discussed by van Beusekom et al. (2012) and Kowalski et al. (2013) in the context of connectivity with the open North Sea and influences of eutrophication and sedimentology. They suggested that the organic matter turnover in the entire Wadden Sea is governed by organic matter import from the North Sea, but that regionally different eutrophication effects as well as sediment compositions modulate this general pattern. The reason for regional differences may be related to the shape and size of the individual tidal basins. van Beusekom et al. (2012) found that wider tidal basins with a large distance between barrier islands and mainland, as is the case in the North Frisian Wadden Sea, generally have a lower eutrophication status than narrower basins predominating in the East Frisian Wadden Sea. Together with the high water exchange rate the accumulation of organic matter is reduced in the North Frisian Wadden Sea and the oxygen demand per volume is lower than in the more narrow eutrophicated basins. Therefore, aerobic degradation of organic matter dominated in the North Frisian Wadden Sea, where the distance between barrier islands and mainland is large. ~~on export magnitude~~This leads to less TA production (in relation to DIC production) than in the East Frisian Wadden Sea, where anaerobic degradation of organic matter dominated in more restricted tidal basins.

~~Observed high TA and DIC concentrations in the SE North Sea are mainly caused by TA and DIC export from the Wadden Sea (Fig.3-5). TA concentrations could be better reproduced than DIC concentrations in the model experiments, which was mainly due to the higher~~

~~sensitivity of DIC to modelled biology. Nevertheless, from a present point of view the Wadden Sea is the main driver of TA concentrations in the German Bight. Future forecast studies of the evolution of the carbonate system in the German Bight will have to specifically focus on the Wadden Sea and on processes occurring there. In this context the Wadden Sea evolution during future sea level rise is the most important factor. The balance between sediment supply from the North Sea and sea level rise is a general precondition for the persistence of the Wadden Sea (Flemming and Davis, 1994; Van Koningsveld et al., 2008). An accelerating sea level rise could lead to a deficient sediment supply from the North Sea and shift the balance at first in the largest tidal basins and at last in the smallest basins. (CPSL, 2001; Van Goor et al., 2003). The share of intertidal flats as potential sedimentation areas is larger in smaller tidal basins (van Beusekom et al., 2012), whereas larger basins have a larger share of subtidal areas. Thus, assuming an accelerating sea level rise, large tidal basins will turn into lagoons, while tidal flats may still exist in smaller tidal basins. This effect could decrease the overall Wadden Sea export rates of TA, because sediments would no longer be exposed to the atmosphere and the products of sulphate reduction would reoxidise in the water column. Moreover, benthic-pelagic exchange in the former intertidal flats would only be diffusive and no longer advective due to hydraulic gradients during ebb tides, when parts of the sediment become unsaturated with water. Caused by changes in hydrography and sea level the sedimentological composition may also change. If sediments become more sandy, aerobic degradation of organic matter is likely to become more dominant (de Beer et al., 2004). Regionally, the North Frisian Wadden Sea will be more affected by rising sea level because there the tidal basins are larger than the tidal basins in the East Frisian Wadden Sea and even larger than the inner Jade Bay.~~

~~The Wadden Sea export of TA and DIC is driven by the turnover of organic material. Decreasing anthropogenic eutrophication can lead to decreasing phytoplankton biomass and production (Cadée & Hegeman, 2002; van Beusekom et al., 2009). Thus, the natural variability of the North Sea primary production becomes more important in determining the organic matter turnover in the Wadden Sea (McQuatters-Gollop et al., 2007; McQuatters-Gollop & Vermaat, 2011). Moreover, despite the assumption of decreasing overall TA export rates from the Wadden Sea the impact of the North Frisian Wadden Sea on the carbonate system of the German Bight could potentially change due to a change of tidal prisms and~~

~~thus a change in imported organic matter. If less organic matter is remineralised in the North Frisian Wadden Sea, less TA and DIC will be exported to the North Sea.~~

~~In the context of climate change, processes that have impact on the freshwater budget of tidal mud flats will gain in importance. Future climate change will have an impact in coastal hydrology due to changes in ground water formation rates (Faneca Sànchez et al., 2012; Sulzbacher et al., 2012), that may change both surface and subterranean run-off into the North Sea. An increasing discharge of small rivers and groundwater into the Wadden Sea is likely to increase DIC, TA, and possibly nutrient loads and may enhance the production of organic matter. Evaporation could also increase due to increased warming and become a more important process than today (Onken & Riethmüller, 2010).~~

~~Concluding, in the course of climate change the North Frisian Wadden Sea will be affected first by sea level rise, which will result in decreased TA and DIC export rates due to less turnover of organic matter there. This could lead to a decreased buffering capacity in the German Bight for atmospheric CO_2. Overall, less organic matter will be remineralised in the Wadden Sea.~~

4.3. TA budgets and variability of TA mass in the German Bight

Modelled TA and DIC concentrations in the German Bight have a high interannual and seasonal variability (Fig. 8). The interannual variability of the model results are mainly driven by the physical prescribed environment. Overall, the TA variability is more sensitive to Wadden Sea export rates than DIC variability, because the latter is dominated by biological processes. However, the ~~implementation~~inclusion of Wadden Sea DIC export rates ~~enabled a better reproduction of~~improved correspondence with observed DIC concentrations in the near-coastal North Sea.

It is a logical step to attribute the TA variability to variabilities of the different sources. In order to calculate a realistic budget, scenario B was considered. Annual and seasonal budgets of TA sources and sinks in this scenario are shown in Table ~~2~~6. Note that Riv_{eff} is not taken into account for the budget calculations. This is explained in the Method Section “River Input”.

Comparing the absolute values of all sources and sinks of the mean year results in a relative ranking of the processes. 41 % of all TA mass changes in the validation area were due to river loads, 37 % were due to net transport, 16 % were due to Wadden Sea export rates, 6 % were due to internal processes. River input ranged from 78 to 152 Gmol TA yr^{-1} and had the highest absolute variability of all TA sources in the validation area. This is mostly due to the high variability of annual freshwater discharge, which is indicated by low (negative) values of Riv_{eff}. The latter values show that the riverine TA loads together with the freshwater flux induce a small dilution of TA in the validation area for each year. ~~Comparing the absolute values of all sources and sinks of the mean year (only non-leap years were used) results in a relative ranking of the processes. 63 % of all TA mass changes in the validation area were due to net transport, 25 % were due to Wadden Sea export rates, 9 % were due to internal processes, and 3 % were due to river input Riv_{eff} of TA (see chapter 2.6.2).~~ Certainly, this ranking depends mainly on the characteristics of the Elbe estuary. Due to the high concentration of TA in rivers Rhine and Meuse (Netherlands) they had an effective river input of +24 Gmol TA yr^{-1} in 2008, which constitutes a much greater impact on TA concentration changes than the Elbe river. In a sensitivity test, we switched off the TA loads of rivers Rhine and Meuse for the year 2008 and found that the net flow of -71 Gmol TA yr^{-1} decreased to -80 Gmol TA yr^{-1}, which indicates that water entering the validation box from the western boundary is less TA-rich in the test case than in the reference run.

At seasonal time scales (Table ~~2~~6 lower part) the net transport dominated the variations from October to March, while internal processes play a more important role from April to June (~~47~~28 %). The impact of effective river input was ~~smaller~~less than ~~10~~5% in every quarter. The Wadden Sea TA export rates had an impact of ~~59~~36 % on TA mass changes in the validation area from July to September. Note that these percentages are related to the sum of the absolute values of the budgeting terms.

Summing up the sources and sinks, Wadden Sea exchange rates, internal processes and effective river loads resulted in highest sums in 2002 and 2003 (51 and 52 Gmol TA yr^{-1}) and lowest in 2009 (44 Gmol TA yr^{-1}). For the consideration of TA variation we excluded net transport and actual river loads, because these fluxes are diluted and do not necessarily change the TA concentrations. In agreement with this, the highest TA concentrations were simulated in summer 2003 (Fig. 8). The high interannual variability of summer concentrations was driven essentially by hydrodynamic differences between the years. Flushing times and their interannual variability were higher in summer than in winter (Fig. 6) of every year. High flushing times or less strong circulation do have an accumulating effect on exported TA in the validation area. To understand the reasons of the different flushing times monthly stream patterns were analysed (Fig. 7). Distinct anticlockwise stream patterns defined the hydrodynamic conditions in every winter. Summer stream patterns were in most years weaker, especially in the German Bight (compare Fig. 7, June 2003). In August 2003 the eastern part of the German Bight shows a clockwise rotation, which transports TA-enriched water from July back to the Wadden-Sea area for further enrichment. This could explain the highest concentrations in summer 2003.

~~One aim of this study was to recalculate the Wadden Sea TA export rates calculated by~~ Thomas et al. (2009~~). They~~) estimated that 73 Gmol TA yr^{-1} were produced in the Wadden Sea. Their calculations were based on measurements in 2001 and 2002. The presented model was validated with data measured in August 2008 (Salt et al., 2013) at the same positions. High TA concentrations in the German Bight were observed in summer 2001 and in summer 2008. Due to the scarcity of data, the West Frisian Wadden Sea was not considered in the simulations, but, as the western area is much larger than the eastern area, the amount of exported TA from that area can ~~safely~~ be assumed to be in the same range as from the East Frisian Wadden Sea (10 to 14 Gmol TA yr^{-1}). With additional export from the West Frisian Wadden Sea, the maximum overall Wadden Sea export may be as high as 53 Gmol TA yr^{-1}. Thus, the TA export from the Wadden Sea calculated in this study is 20 to 34 TA Gmol yr^{-1} lower than that assumed in the study of Thomas et al. (2009). This is mainly due to the flushing time that was assumed by Thomas et al. (2009). They considered the water masses to be flushed within six weeks (Lenhart et al., 1995). Flushing times calculated in the present study were significantly longer and more variable in summer. Since the Wadden Sea export calculated by Thomas et al. (2009) was defined as a closing term ~~of~~for the TA budget, underestimated summerly flushing times led to an overestimation of the exchange with the adjacent North Sea.

Table 4 shows that our scenario B underestimates the observed TA concentration by about 5.1 µmol kg^{-1} in 2008. Scenario A has lower TA concentration than scenario B in the validation area. The difference is about 11 µmol kg^{-1}. This means that the Wadden Sea export of 39 Gmol TA yr^{-1} results in a concentration difference of 11 µmol kg^{-1}. Assuming linearity, the deviation between scenario B and the observations (5.1 µmol kg^{-1}) would be compensated by an additional Wadden Sea export of about 18 Gmol TA yr^{-1}. If we assume that the deviation between observation and scenario B is entirely due to uncertainties or errors in the Wadden Sea export estimate, then the uncertainty of this export is 18 Gmol TA yr^{-1}.

Another problematic aspect in the TA export estimate by Thomas et al. (2009) is the fact that their TA budget merges the sources of anaerobic TA generation from sediment and from the Wadden Sea into a single source “anaerobic processes in the Wadden Sea”. Burt et al. (2014) found a sediment TA generation of 12 mmol TA m^{-2} d^{-1} at one station in the German Bight based on Ra-measurements. This fits into the range of microbial gross ~~sulfate~~sulphate reduction rates ~~measured~~reported by Al-Raei et al. (2009) in the backbarrier tidal areas of Spiekeroog island, and by Brenner et al. (2016) at the Dutch coast. Within the latter paper, the different sources of TA from the sediment were quantified. The largest term was benthic calcite dissolution, which would be cancelled out in terms of TA generation assuming a steady-state compensation by biogenic calcite production. Extrapolating the southern North Sea TA generation (without calcite dissolution) from the data for one station of Brenner et al. (2016) results in an annual TA production of 12.2 Gmol in the German Bight (Area = 28.415 km^{2}). This is ~~surely~~likely an upper limit of sediment TA generation, as the measurements were done in summer when seasonal fluxes are maximal. This calculation reduces the annual Wadden Sea TA generation estimated by Thomas et al. (2009) from 73 to ~~60.8~~61 Gmol, which is still higher than our present estimate. In spite of the unidentified additional TA-fluxes, both the estimate by Thomas et al. (2009) and our present model-based quantification confirm the importance of the Wadden-Sea export fluxes of TA on the North Sea carbonate system at present and in the future.

4.4. The impact of exported TA and DIC on the North Sea and influences on export magnitude

Observed high TA and DIC concentrations in the SE North Sea are mainly caused by TA and DIC export from the Wadden Sea (Fig.3-5). TA concentrations could be better reproduced than DIC concentrations in the model experiments, which was mainly due to the higher sensitivity of DIC to modelled biology. Nevertheless, from a present point of view the

Wadden Sea is the main driver of TA concentrations in the German Bight. Future forecast studies of the evolution of the carbonate system in the German Bight will have to specifically focus on the Wadden Sea and on processes occurring there. In this context the Wadden Sea evolution during future sea level rise is the most important factor. The balance between sediment supply from the North Sea and sea level rise is a general precondition for the persistence of the Wadden Sea (Flemming and Davis, 1994; van Koningsveld et al., 2008). An accelerating sea level rise could lead to a deficient sediment supply from the North Sea and shift the balance at first in the largest tidal basins and at last in the smallest basins. (CPSL, 2001; van Goor et al., 2003). The share of intertidal flats as potential sedimentation areas is larger in smaller tidal basins (van Beusekom et al., 2012), whereas larger basins have a larger share of subtidal areas. Thus, assuming an accelerating sea level rise, large tidal basins will turn into lagoons, while tidal flats may still exist in smaller tidal basins. This effect could decrease the overall Wadden Sea export rates of TA, because sediments would no longer be exposed to the atmosphere and the products of sulphate reduction would reoxidise in the water column. Moreover, benthic-pelagic exchange in the former intertidal flats would be more diffusive and less advective then today due to hydraulic gradients during ebb tides, when parts of the sediment become unsaturated with water. This would decrease TA export into the North Sea. Caused by changes in hydrography and sea level the sedimentological composition may also change. If sediments become more sandy, aerobic degradation of organic matter is likely to become more important (de Beer et al., 2005). In fine grained silt diffusive transport plays a key role, while in the upper layer of coarse (sandy) sediments advection is the dominant process. Regionally, the North Frisian Wadden Sea will be more affected by rising sea level because there the tidal basins are larger than the tidal basins in the East Frisian Wadden Sea and even larger than the inner Jade Bay.

The Wadden Sea export of TA and DIC is driven by the turnover of organic material. Decreasing anthropogenic eutrophication can lead to decreasing phytoplankton biomass and production (Cadée & Hegeman, 2002; van Beusekom et al., 2009). Thus, the natural variability of the North Sea primary production becomes more important in determining the organic matter turnover in the Wadden Sea (McQuatters-Gollop et al., 2007; McQuatters-Gollop & Vermaat, 2011). pH values in Dutch coastal waters decreased from 1990 to 2006 drastically. Changes in nutrient variability were identified as possible drivers (Provoost et al., 2010), which is consistent with model simulations by Borges and Gypens (2010). Moreover, despite the assumption of decreasing overall TA export rates from the Wadden Sea the impact of the North Frisian Wadden Sea on the carbonate system of the German Bight could potentially adjust to a change of tidal prisms and thus a modulation in imported organic matter. If less organic matter is remineralised in the North Frisian Wadden Sea, less TA and DIC will be exported into the North Sea.

In the context of climate change, processes that have impact on the freshwater budget of tidal mud flats will gain in importance. Future climate change will have an impact in coastal hydrology due to changes in ground water formation rates (Faneca Sànchez et al., 2012; Sulzbacher et al., 2012), that may change both surface and subterranean run-off into the North Sea. An increasing discharge of small rivers and groundwater into the Wadden Sea is likely to increase DIC, TA, and possibly nutrient loads and may enhance the production of organic matter. Evaporation could also increase due to increased warming and become a more important process than today (Onken & Riethmüller, 2010), as will methane cycling change due to nutrient changes, sea level and temperature rise (e.g., Höpner and Michaelis, 1994; Akam et al., 2020).

Concluding, in the course of climate change the North Frisian Wadden Sea will be affected first by sea level rise, which will result in decreased TA and DIC export rates due to less turnover of organic matter there. This could lead to a decreased buffering capacity in the German Bight for atmospheric CO_2. Overall, less organic matter will be remineralised in the Wadden Sea.

~~5.4 TA / DIC ratios during the course of the year~~

~~The overall (bulk) export rates for the Wadden Sea were calculated for DIC and TA as well in the present study. Although the detailed processes in all compartments were not simulated explicitly, the ratio of exported TA and DIC reflects the dominant underlying biogeochemical processes (Chen & Wang, 1999; Zeebe & Wolf-Gladrow, 2001; Thomas et al. 2009; Sippo et al., 2016; Wurgaft et al., 2019). Aerobic degradation of organic material results in a reduction of TA due to both increasing nitrate and DIC concentrations, and is indicated by a TA / DIC ratio of -0.16. Denitrification is indicated by a TA / DIC ratio of 1 and anaerobic processes related to sulphate reduction of organic material are indicated by a TA / DIC ratio of 2. Aerobic and anaerobic oxidation of upward diffusing methane would further~~

~~impact the TA / DIC ratio in opposite directions, but were not considered in the present study.~~

~~The ratios of the export rates TA / DIC for the different export areas are depicted in Fig. 9. The pelagic TA / DIC ratio in the North Frisian Wadden Sea (NF) ranged between 0 and 0.5 in spring and summer. Aerobic degradation of organic material and denitrification were the dominant processes here. The ratio became negative in autumn, which was due to a negative ΔTA value and thus a consumption of TA (compare Tab. 1). This may reflect resuspension of the surface sediment due to increasing wind-induced hydrodynamic circulation, so that previously formed sedimentary pyrite was re-oxidized (e.g., Kowalski et al., 2013). The DIC export rate also had its minimum in autumn (Tab. 1), which was likely caused by a decreasing supply of organic material during this season (e.g., Kowalski et al., 2009).~~

~~The TA / DIC ratios in the Jade Bay were around 1 between January and April, but ranged between 1.5 and 2 from June until September, when sulphate reduction associated with organic matter and/or methane oxidation and pyrite burial became the dominant processes. Later in the year, the ratio decreased to -0.5 in autumn, when aerobic degradation and re-oxidation of pyrite may have occurred, promoted by increasing wind forces and associated re-suspension and sulphide oxidation of anoxic sediment layers (Kowalski et al., 2013). The DIC export rate had its minimum in autumn, again due to limited supply of organic matter (Tab. 1).~~

~~The TA / DIC ratio of the East Frisian Wadden Sea was about 1 in February, when denitrification dominated. A slightly negative ratio was found at the beginning of April when aerobic degradation of organic matter dominated. Denitrification dominated until June. In August the ratio increased to 2, because anaerobic degradation processes became more important. Afterwards the ratios increased up to 3 in autumn, mainly due to relatively high ΔTA values (16 µmol kg^{-1}) compared to ΔDIC values (5 µmol kg^{-1}) (compare Tab. 1). This was caused by dominating processes related to organotrophic sulphate reduction. The maximum ratio of 3 may reflect a short-term effect of iron reduction that influenced the measurements of TA concentrations. Iron reduction leads to a high generation of TA on only short time scales, because reduced iron is rapidly re-oxidised to lower TA.~~

~~Based on these results, the North Frisian Wadden Sea export area showed a different pattern when compared to the East Frisian Wadden Sea and the Jade Bay areas. Aerobic degradation of organic matter played a key role in the North Frisian Wadden Sea during spring and summer. The DIC export rates indicate that most organic matter was degraded there, which may have been controlled by higher daily exchanged water masses in the North Frisian (8.1 km^3 d^{-1}) than in the East Frisian Wadden Sea (2.3 km^3 d^{-1}) and in the Jade Bay (0.8 km^3 d^{-1}) (compare Tab. 3). On the other hand, TA export rates of the North Frisian and the East Frisian Wadden Sea were in the same range. Regional differences in organic matter dynamics in the Wadden Sea have already been discussed by van Beusekom et al. (2012). They suggested that the organic matter turnover in the Wadden Sea is overall driven by OM import from the North Sea, but that regionally different eutrophication effects modulate the general pattern. The reason for these differences is related to the shape and size of the individual tidal basins. Van Beusekom et al. (2012) proposed that wider tidal basins with a large distance between barrier islands and mainland generally have a lower eutrophication status than narrower ones. This may lead to a "dilution" effect of the imported organic matter in wider tidal basins.~~ ~~Therefore, aerobic degradation of organic matter dominated in the North Frisian Wadden Sea, where the distance between barrier islands and mainland is large.~~ ~~This leads to less eutrophication than in the East Frisian Wadden Sea, where anaerobic degradation of organic matter dominated in more restricted tidal basins.~~

~~5.~~5 Conclusion and Outlook

We ~~presented~~present a budget calculation of TA sources in the German Bight and ~~related 25~~relate 16 % of the annual TA mass changes to ~~Wadden Sea~~TA exports ~~of TA~~from the Wadden Sea. The impact of riverine bulk TA is less important in the German Bight than the contribution from the Wadden Sea due to the comparatively low TA concentrations in the Elbe estuary. ~~Nevertheless, the rivers are sources of allochthonous nitrate, and denitrification of which in sediments is a major source for net TA generation.~~

The evolution of the carbonate system in the German Bight under future anthropogenic or climate change depends on the evolution of the Wadden Sea. The amount of TA and DIC that is exported from the Wadden Sea depends on the amount of organic matter that is imported from the North Sea and remineralised in the Wadden Sea. Decreasing riverine nutrient loads have led to decreasing phytoplankton biomass and production (Cadée & Hegeman, 2002; van Beusekom et al., 2009), a trend that is expected to continue~~.~~ (European Water Framework Directive). However, altered natural dynamics of nutrient cycling and productivity can override the decreasing riverine nutrient loads (van Beusekom et al., 2012), but these will not generate TA in the magnitude of denitrification of riverborne nitrate.

In the context of sea level rise, the North Frisian Wadden Sea will potentially be more affected by a loss of intertidal areas than the East Frisian Wadden Sea (van Beusekom et al., 2012). This effect is likely to reduce the turnover of organic material in this sector of the Wadden Sea, which will decrease TA production and decrease the overall input into the southern North Sea.

Thomas et al. (2009) estimated that the Wadden Sea facilitates approximately 7 – 10% of the annual CO_2 uptake of the North Sea. This is motivation for model studies on the future role of the Wadden Sea in the CO_2 balance of the North Sea under regional climate change. Future research will also have to address the composition and amount of submarine ground water discharge, as well as the magnitude and seasonal dynamics in discharge and composition of small water inlets at the coast which are currently ignored due to a lacking data base.

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Tables

Table 1: Mean TA and DIC concentrations [µmol ~~kg~~l^{-1}] during rising and falling water levels and the respective differences (Δ-values) that were used as wad_sta in (1). Areas are the North Frisian (~~NF~~N), the East Frisian (~~EF~~E) Wadden Sea and the Jade Bay (~~JB~~J).

Area	Date	TA (rising)	TA (falling)	ΔTA	DIC (rising)	DIC (falling)	ΔDIC
~~NF~~N	29.04.2009	2343	2355	12	2082*	2106	24
	17.06.2009	2328	2332	4	2170	2190	20
	26.08.2009	2238	2252	14	2077	2105	28
	05.11.2009	2335	2333	-2	2205	2209	4
~~JB~~J	20.01.2010	2429	2443	14	2380	2392	12
	21.04.2010	2415	2448	33	2099	2132	33
	26.07.2010	2424	2485	61	2159	2187	28
	09.11.2010	2402	2399	-3	2302	2310	8
~~EF~~E	03.03.2010	2379	2393	14	2313	2328	15
	07.04.2010	2346	2342	-4	2068	2082	14
	17./18.05.2011	2445	2451	6	2209	2221	12
	20.08.2002	2377	2414	37	2010	2030	20
	01.11.2010	2423	2439	16	2293	2298	5

*: This value was estimated.

~~Table 2: Annual TA budgets in the validation area of the years 2001 to 2009 and seasonal budgets of the non-leave average years from January to March, April to June, July to September and October to December [Gmol]. Net Flow is the amount of TA that passes the validation area.~~Table 2~~Negative values indicate a net export from the validation area to the adjacent North Sea. Δcontent indicates the difference of the TA contents of the last and the first time steps of the simulated year or quarter.~~

~~-~~	~~Wadden Sea~~	~~internal processes~~	~~river loads~~	~~Riv$_{eff}$~~	~~net flow~~	~~Δcontent~~
	~~Gmol/yr~~	~~Gmol/yr~~	~~Gmol/yr~~	~~Gmol/yr~~	~~Gmol/yr~~	~~Gmol~~
~~2001~~	~~39~~	~~13~~	~~87~~	~~-5~~	~~38~~	~~177~~
~~2002~~	~~39~~	~~19~~	~~152~~	~~-7~~	~~-223~~	~~-13~~
~~2003~~	~~39~~	~~16~~	~~91~~	~~-3~~	~~-98~~	~~48~~
~~2004~~	~~39~~	~~13~~	~~78~~	~~-5~~	~~-8~~	~~122~~
~~2005~~	~~39~~	~~12~~	~~89~~	~~-5~~	~~-98~~	~~42~~
~~2006~~	~~39~~	~~12~~	~~88~~	~~-4~~	~~-56~~	~~83~~
~~2007~~	~~39~~	~~12~~	~~110~~	~~-5~~	~~-132~~	~~29~~
~~2008~~	~~39~~	~~14~~	~~93~~	~~-5~~	~~-71~~	~~75~~
~~2009~~	~~39~~	~~10~~	~~83~~	~~-5~~	~~-151~~	~~-19~~
~~t = 3 mon~~	~~Gmol/t~~	~~Gmol/t~~	~~Gmol/t~~	~~Gmol/t~~	~~Gmol/t~~	~~Gmol~~
~~Jan - Mar~~	~~8~~	~~-1~~	~~38~~	~~-1~~	~~-57~~	~~-12~~
~~Apr - Jun~~	~~10~~	~~14~~	~~23~~	~~-2~~	~~4~~	~~51~~
~~Jul - Sep~~	~~17~~	~~-2~~	~~15~~	~~-2~~	~~8~~	~~38~~
~~Oct - Dec~~	~~4~~	~~2~~	~~24~~	~~0~~	~~-58~~	~~-28~~

~~Table 3~~: Daily Wadden Sea runoff to the North Sea at different export areas.

Position	wad_exc [10^6 m^3 d^{-1}]
N1	273
N2	1225
N3	1416
N4	1128
N5	4038
N6	18
J1 - J3	251
E1	380
E2	634
E3	437
E4	857

Table 3~~Table 4: Averages (µmol kg^{-1}), standard deviations (µmol kg^{-1}), RMSE (µmol kg^{-1}), and correlation coefficients r for the observed TA concentrations and the corresponding scenarios A and B within the validation area.~~

~~TA~~	~~Average~~	~~Stdv~~	~~RMSE~~	~~r~~
~~Obs~~	~~2333.52~~	~~32.51~~		
~~A~~	~~2327.64~~	~~6.84~~	~~27.97~~	~~0.77~~
~~B~~	~~2338.60~~	~~22.09~~	~~18.34~~	~~0.86~~

~~Table 5: Averages (µmol kg^{-1}), standard deviations (µmol kg^{-1}), RMSE (µmol kg^{-1}), and correlation coefficients r for the observed DIC concentrations and the corresponding scenarios A and B within the validation area.~~

~~DIC~~	~~Average~~	~~Stdv~~	~~RMSE~~	~~r~~
~~Obs~~	~~2107.05~~	~~24.23~~		
~~A~~	~~2080.93~~	~~14.24~~	~~43.48~~	~~-0.64~~
~~B~~	~~2091.15~~	~~9.25~~	~~25.87~~	~~0.55~~

~~Table 6~~: Examples for the carbonate system composition of small fresh water inlets draining into the Jade Bay and the backbarrier tidal area of Spiekeroog Island, given in (µmol kg^{-1}). ~~Winter~~Autumn results (~~W~~A) (October 31st, 2010) are taken from Winde et al. (2014); ~~summer~~spring sampling (S) took place on May 20th, 2011.

Site	Position	DIC(~~W~~A)	TA(~~W~~A)	DIC(S)	TA(S)
Neuharlingersiel	53°41.944 N 7°42.170 E	2319	1773	1915	1878
Harlesiel	53°42.376 N 7°48.538 E	3651	3183	1939	1983
Wanger/Horumersiel	53°41.015 N 8°1.170 E	5405	4880	6270	6602
Hooksiel	53°38.421 N 8°4.805 E	2875	3105	3035	3302
Maade	53°33.534 N 8°7.082 E	5047	4448	5960	6228
Mariensiel	53°30.895 N 8°2.873 E	6455	5904	3665	3536
Dangaster Siel	53°26.737N 8°6.577 E	1868	1246	1647	1498
Wappelersiel	53°23.414 N 8°12.437 E	1373	630	1358	1152
Schweiburger Siel	53°24.725 N 8°16.968 E	4397	3579	4656	4493
Eckenwarder Siel	53°31.249 N 8°16.527 E	6542	6050	2119	4005

Table 4: Averages (µmol kg^{-1}), standard deviations (µmol kg^{-1}), RMSE (µmol kg^{-1}), and correlation coefficients r for the observed TA concentrations and the corresponding scenarios A and B within the validation area.

TA	Average	Stdv	RMSE	r
Obs 2008	2333.52	32.51		
Obs 2005	2332.09	21.69		
Obs 2001	2333.83	33.19		
Sim A 2008	2327.64	6.84	27.97	0.77
Sim A 2005	2322.16	5.21	22.05	0.45
Sim A 2001	2329.79	5.32	31.89	0.24
Sim B 2008	2338.60	22.09	18.34	0.86
Sim B 2005	2339.48	26.81	31.81	0.18
Sim B 2001	2342.96	17.28	30.07	0.47

Table 5: Averages (µmol kg^{-1}), standard deviations (µmol kg^{-1}), RMSE (µmol kg^{-1}), and correlation coefficients r for the observed DIC concentrations and the corresponding scenarios A and B within the validation area.

DIC	Average	Stdv	RMSE	r
Obs 2008	2107.05	24.23		
Obs 2005	2098.20	33.42		
Obs 2001	2105.49	25.21		
Sim A 2008	2080.93	14.24	43.48	-0.64
Sim A 2005	2083.53	21.94	26.97	0.73
Sim A 2001	2077.53	17.61	38.89	0.22
Sim B 2008	2091.15	9.25	25.87	0.55
Sim B 2005	2101.26	10.97	33.96	0.10
Sim B 2001	2092.69	11.71	25.33	0.48

Table 6: Annual TA budgets in the validation area of the years 2001 to 2009, annual averages and seasonal budgets of from January to March, April to June, July to September and October to December [Gmol]. Net Flow is the annual net TA transport across the boundaries of the validation area. Negative values indicate a net export from the validation area to the adjacent North Sea. Δcontent indicates the difference of the TA contents between the last and the first time steps of the simulated year or quarter.

	Wadden Sea export	internal processes	river loads	Riv$_{eff}$	net flow	Δcontent
	Gmol/yr	Gmol/yr	Gmol/yr	Gmol/yr	Gmol/yr	Gmol
2001	39	13	87	-5	38	177
2002	39	19	152	-7	-223	-13
2003	39	16	91	-3	-98	48
2004	39	13	78	-5	-8	122
2005	39	12	89	-5	-98	42
2006	39	12	88	-4	-56	83
2007	39	12	110	-5	-132	29
2008	39	14	93	-5	-71	75
2009	39	10	83	-5	-151	-19
Average	Gmol/yr	Gmol/yr	Gmol/yr	Gmol/yr	Gmol/yr	Gmol
	39	14	101	-5	-89	65
t = 3 mon	Gmol/t	Gmol/t	Gmol/t	Gmol/t	Gmol/t	Gmol

Jan - Mar	7	-1	38	-1	-49	-5
Apr - Jun	10	15	23	-2	6	54
Jul - Sep	17	-2	15	-2	13	43
Oct - Dec	4	1	25	0	-56	-26

6. Figure ~~Caption~~Captions

~~Figure 1~~Figure 1: Upper panel: Map of the southeastern North Sea and the bordering land. Lower panel: Model domains of ECOHAM (red) and FVCOM (blue), positions of rivers 1 – 16 (left, see Table 2) and the Wadden Sea export areas grid cells (right). The ~~green~~magenta edges identify the validation area, western and eastern part separated by the ~~green~~magenta dashed line.

Figure 2: Monthly Wadden Sea export of DIC and TA [Gmol mon^{-1}] at the North Frisian coast (~~NF~~N), East Frisian coast (~~EF~~E) and the Jade Bay in scenario B. The export rates were calculated for DIC and TA based on measured concentrations and simulated water fluxes.

Figure 3: Surface TA~~-~~ concentrations [µmol TA kg^{-1}] in August 2008 observed (a) and simulated with scenario A (b) and B (c). The black lines indicate the validation box.

~~Figure 4: Surface DIC-concentrations [µmol DIC kg^{-1}] in August 2008 observed (a) and simulated with scenario A (b) and B (c).~~

~~Figure 5~~Figure 4: Differences between TA surface summer observations and results from scenario A (a) and B (b) and the differences between DIC surface observations and results from scenario A (c) and B (d), all in µmol kg^{-1}. The black lines indicate the validation box.

Figure 5: Surface DIC concentrations [µmol DIC kg^{-1}] in August 2008 observed (a) and simulated with scenario A (b) and B (c). The black lines indicate the validation box.

Figure 6: Flushing times in the validation area in summer (June to August) and winter (January to March). The whole validation area is represented in blue, green is the western part of the validation area (4.5°E to 7°E) and red is the eastern part (east of 7°E).

Figure 7: Monthly mean simulated streamlines for summer months 2003 and 2008.

Figure 8: Simulated monthly mean concentrations of TA (scenario A (a), scenario B (b)) [µmol TA kg^{-1}] and DIC (scenario A (c), scenario B (d)) [µmol DIC kg^{-1}] in the validation area for the years 2001-2009.

Fig. 9: ~~Temporal~~Temporally interpolated TA/DIC ratio of the export rates in the North Frisian, East Frisian, and Jade Bay. These ratios are calculated using the Δ-values of Table 1.

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8. Appendix

Table A1: Annual riverine freshwater discharge [km³ yr⁻¹]. The numbering refers to Fig. 1.

	2001	2002	2003	2004	2005	2006	2007	2008	2009
1) Elbe	23.05	43.38	23.95	19.56	25.56	26.98	26.61	24.62	24.28
2) Ems	3.47	4.48	3.15	3.52	2.99	2.54	4.32	3.32	2.58
3) Noordzeekanaal	3.21	2.98	2.49	3.05	3.03	2.96	1.55	3.05	2.46
4) Ijsselmeer (east)	9.55	9.94	6.27	7.97	7.35	7.30	9.10	8.23	6.59
5) Ijsselmeer (west)	9.55	9.94	6.27	7.97	7.35	7.30	9.10	8.23	6.59
6) Nieuwe Waterweg	50.37	51.33	34.72	42.91	41.61	44.21	49.59	49.76	44.69
7) Haringvliet	33.10	35.18	17.92	10.77	12.36	16.02	24.00	15.70	11.06
8) Scheldt	7.28	2.74	4.31	3.64	3.59	3.74	4.63	4.57	3.63
9) Weser	11.43	18.97	11.80	10.52	10.37	9.72	16.21	12.59	9.58
10) Firth of Forth	2.72	3.76	2.06	3.01	3.00	2.84	2.85	3.59	3.66
11) Tyne	1.81	2.25	1.18	2.04	1.92	1.78	2.09	2.70	2.05
12) Tees	1.33	1.78	0.94	1.59	1.27	1.45	1.49	1.99	1.55
13) Humber	10.76	12.10	7.16	10.51	7.68	11.11	12.03	13.87	9.60
14) Wash	5.46	4.39	3.08	3.91	1.96	2.72	5.24	4.77	3.21
15) Thames	4.47	3.23	2.41	2.13	0.96	1.57	3.52	3.20	2.38
16) Eider	0.67	0.97	0.47	0.70	0.68	0.67	0.63	0.58	0.57
Sum	178.2	207.4	128.1	133.7	131.6	142.9	172.9	160.7	134.4

Table A2: River numbers in Fig. 1, their positions and source of data

Number in Fig. 1	Name	River mouth position	Data source
1	Elbe	53°53'20"N 08°55'00" E	Pätsch & Lenhart (2008); TA-, DIC- and nitrate-concentrations by Amann (2015)
2	Ems	53°29'20"N 06°55'00"E	Pätsch & Lenhart (2008)
3	Noordzeekanaal	52°17'20"N 04°15'00"E	Pätsch & Lenhart (2008); TA-, DIC- and nitrate-concentrations from waterbase.nl
4	Ijsselmeer (east)	53°17'20"N 05°15'00"E	As above
5	Ijsselmeer (west)	53°05'20"N 04°55'00"E	As above
6	Nieuwe Waterweg	52°05'20"N 03°55'00"E	As above
7	Haringvliet	51°53'20"N 03°55'00"E	As above
8	Scheldt	51°29'20"N 03°15'00"E	As above
9	Weser	53°53'20"N 08°15'00"E	Pätsch & Lenhart (2008)
10	Firth of Forth	56°05'20"N 02°45'00"W	HASEC (2012)
11	Tyne	55°05'20"N 01°25'00"W	HASEC (2012)
12	Tees	54°41'20"N 01°05'00"W	HASEC (2012)
13	Humber	53°41'20"N 00°25'00"W	HASEC (2012)
14	Wash	52°53'20"N 00°15'00"E	HASEC (2012): sum of 4 rivers: Nene, Ouse, Welland and Witham
15	Thames	51°29'20"N 00°55'00"E	HASEC (2012)
16	Eider	54°05'20"N 08°55'00"E	Johannsen et al, 2008

-Table A3: ~~Values~~Monthly values of TA, DIC and NO_3 concentrations [µmol kg^{-1}] of rivers, the annual mean and the standard deviation

River parameter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	~~mean~~Mean	SD
Elbe TA	2380	2272	2293	2083	2017	1967	1916	1768	1988	2156	2342	2488	2139	218
Noordzeekanaal TA	3762	3550	3524	3441	4748	3278	3419	3183	3027	3299	3210	3413	3488	441
Nieuwe Waterweg TA	2778	2708	2765	3006	2883	2658	2876	2695	2834	2761	2834	2927	2810	102
Haringvliet TA	2588	2635	2532	3666	2826	2829	2659	2660	2496	2816	2758	2585	2754	309
Scheldt TA	3781	3863	3708	3725	3758	3626	3722	3514	3367	3666	3825	3801	3696	140
Ijsselmeer TA	2829	3005	2472	2259	2611	1864	1672	1419	1445	2172	2286	2551	2215	521
Elbe DIC	2415	2319	2362	2179	2093	2025	1956	1853	2018	2200	2428	2512	2197	211
Noordzeekanaal DIC	3748	3579	3470	3334	3901	3252	3331	3136	2977	3214	3183	3405	3378	264
Nieuwe Waterweg DIC	2861	2794	2823	2991	2879	2657	2886	2706	2828	2773	2907	3036	2845	108
Haringvliet DIC	2673	2735	2600	3661	2850	2846	2687	2681	2512	2859	2803	2670	2798	292
Scheldt DIC	3798	3909	3829	3737	3704	3592	3705	3490	3316	3648	3733	3868	3694	167
Ijsselmeer DIC	2824	3008	2458	2234	2576	1826	1636	1369	1399	2134	2285	2565	2193	538
Elbe NO_3	247	330	277	225	193	161	129	103	112	157	267	164	197	72
Noordzeekanaal NO_3	150	168	190	118	79	71	64	73	78	92	107	137	111	42
Nieuwe Waterweg NO_3	232	243	231	195	150	140	132	135	113	145	201	220	178	47
Haringvliet NO_3	233	252	218	200	143	144	133	117	128	127	143	228	172	50
Scheldt NO_3	320	341	347	345	243	221	219	215	189	202	190	274	259	63
Ijsselmeer NO_3	136	159	190	192	135	46	20	14	7	18	20	79	85	73

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