

Interactive comment on “The impact of intertidal areas on the carbonate system of the southern North Sea” by Fabian Schwichtenberg et al.

Anonymous Referee #1

Received and published: 16 February 2020

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

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short, the writing can be much sharper. In the specific comments I'll provide examples and suggestions.

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.

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. 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.

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

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on the relevant time scale of processes here.

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. 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.

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? 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) 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. 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). L. 37-38: does the 'net transport' have a particular direction? 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? L. 42-43: "anaerobic degradation dominated" with which pathway? 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

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obviously not the case in many coastal areas. L. 64-67: Also the Baltic Sea is a key example of this; see e.g. Łukawska-Matuszewska (2017) and Gustafsson et al (2019) 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. 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. L. 158: NO₃ data are also presented in this table, but not mentioned here or much discussed in the manuscript. 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. 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 Pätzsch 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. L. 195: "nutrient dynamics" i.e. productivity and decomposition? L. 196: what about atmospheric sulphur deposition? 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. 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. L. 259-260: So

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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. L. 268-269: This belongs in the introduction. Mention all aims clearly there in the last paragraph. Results: Sections 3.1. and 3.2: why do you discuss the validation of DIC and 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. L. 303: what do you mean by “the standard deviation improved”? In scenario A it was lower, i.e. 7 $\mu\text{mol/kg}$. Or do you mean to say that the standard deviation comes closer to that of the observations? L. 348: rather than mentioning high flushing times, I would paraphrase to focus on the low water renewal or long mean residence time. Same in L. 351-352: I would paraphrase to say that highest inflows occurred in winter. L. 354-356: Can't you use a metric to correct for this feature, allowing fairer comparisons? Sections 3.4 and 3.5: Again, I'd suggest to merge these two. L. 385-386: How is this for TA? 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 the 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. 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. L. 397-399: Move to last paragraph of introduction, this aim is not in there yet. 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. L. 424-428: Could you add some suggestions for improvement? L. 431-453: Why is S burial not discussed here? This seems highly relevant, especially on the longer term. L. 435-437: So external NO_3 inputs are not relevant for benthic denitrification? L. 440-441: Why does this compensate the TA generation? Please explain. L. 444-446:

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But how high and relevant is the deposition of these inputs for the TA budget? This is a very qualitative paragraph. 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? L. 478-479: How has the sensitivity of DIC to modelled biology been confirmed? 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. L. 494-496: Thus slower exchange, what would be the effect on the TA export? L. 497-499: Why? 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? 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. 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. 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 ($\text{data}/91 \times 90$ for the first three months). Again, this is a really odd choice that I don't understand. 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. L. 552-556: Where do these percentages come from? If I understand correctly, 47% refers to $14/51 \text{ Gmol/t}$, but this is less than 47%. Similarly for the 59% term, which I assumed was calculated as $17/38 \text{ Gmol/t}$. 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. L. 571-587: What is missing 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

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uncertainties / errors in the Wadden Sea export estimate, what is then the uncertainty in this export? L. 577: “safely” why? Are their characteristics similar enough? Explain. 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? 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. 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. 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). 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 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

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same time. So how can you tell the relative importance of all of them? L. 633: Another example: here you need the processes you initially neglected to explain your results. L. 640-641: How can you know this negative ratio does not result from reoxidation of reduced species? L. 647-648: Finally a mention of time scales, but please cite Hu and Cai (2011) and/or Gustafsson et al (2019) here. 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. 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. L. 681-684: Why? Explain. L. 713: how was this value estimated? What is the uncertainty and how does this uncertainty impact your budget? 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)

Technical comments: L. 51: ‘regional’ is stated twice, please remove the second mentioning L. 63-64: Ben-Yaakov (1973) also is a seminal paper to mention in this context L. 75: change “Netherland” to “the Netherlands” L. 82: it seems that Brenner et al. (2016) and Burt et al. (2016) can also be mentioned here L. 93: The domain of which model? ECOHAM? Should also be clear to readers unfamiliar with Pätsch et al. (2010) 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. L. 98: “water column” point? grid cell? L. 133: a 1996 reference is used for data from 2001-2009? L. 144: “below” where exactly? L. 159: “monthly mean concentrations” also for the years 2001-2009? L. 173-176: please provide units for each of the terms introduced here. L. 182: add direct link to Pangaea reference. L. 183: volume of Exetainer? L. 184: volume of bottle? L. 185: how much HgCl₂ added? L. 188: which batch of CRM was used? L. 189: what were the accuracy and precision? L. 248: add “the model” to “FVCOM” L. 251: why not add E1, N1, etc to Fig 1 for clarity, rather than this description? L. 253: “overall” i.e. cumulative? L. 263: “table 4”. Also in Table 5, although

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I would suggest to merge both tables. L. 280: "TA" add "surface-water" L. 289: add validation box to Fig 5, possibly also to Figs. 3 and 4. L. 291: "standard variation" don't you mean "standard deviation"? L. 298: rephrase to "the model underestimated TA", passive tense seems odd here L. 299-300: change to "the Dutch Frisian Islands" L. 369: "TA-concentration" remove hyphen. L. 395: change to "were also" L. 460: "this would result in an increased TA concentration of 1 $\mu\text{mol/kg}$ " L. 487: "shift the balance" in which direction / with which result? L. 536: "highest variability" in an absolute or a relative sense? L. 554: replace "smaller" by "less" L. 611-612: add "based on measured concentrations and modelled water fluxes" L. 614-615: add Brenner et al (2016 as reference) L. 627: add the TA/DIC ratio of this process (-2). L. 645: don't you mean "organoclastic"? L. 648: add "leading" between "re-oxidised" and "to" 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. L. 725: should be "non-leap years" L. 728: change "of" to "between" Table 2: change first header to "Wadden Sea export" for clarity L. 780: "temporally interpolated" L. 1172: "values of TA, DIC and NO_3 " Table A3: add horizontal lines in between the parameters for clarity. 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. Fig. 6: Add a legend in the figure itself, not only in the caption. Use striped and dotted bars to make black & white friendly Fig. 9: What is the purpose of the dots? Also this plot can easily be made black & white friendly.

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>

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Interactive comment on *Biogeosciences Discuss.*, <https://doi.org/10.5194/bg-2020-24>, 2020.