

Interactive comment on “Sedimentary alkalinity generation and long-term alkalinity development in the Baltic Sea” by Erik Gustafsson et al.

Erik Gustafsson et al.

erik.gustafsson@su.se

Received and published: 25 September 2018

Gustafsson et al. investigated benthic TA generation under low oxygen conditions using a coupled physical-biogeochemical model BALTSEM and a reactive-transport sediment model (RTM). They discovered that Fe sulfide burial accounts for roughly a quarter of "missing" TA that cannot be accounted for using the BALTSEM model, with the rest of the missing TA potentially coming from groundwater and river input. In addition, the authors found that Fe limitation restricts the magnitude of the Fe-S burial produced TA. Using scenario modeling, this anaerobic TA source will become even smaller because of improvement of oxygen conditions and reduced Fe input from land, hence burial of reduced sulfur. As a result, the Baltic Sea will be more prone to the acidification risks. The major concern I have is how representative the RTM model result

Printer-friendly version

Discussion paper



is across the entire Baltic Sea. The authors stated that this model calculation is very expensive if multiple stations are included. It appears that they tried to extrapolate only one station (F80) to the entire Baltic basin where this is "muddy" sediments. It is known that sediments are heterogeneous and the Baltic definitely should not be an exception. Therefore, I question the validity of their data presentation and interpretation based on the RTM model.

Response: The calculated fluxes at F80 were not extrapolated to the muddy areas of the entire Baltic Sea. Instead, we use it to represent muddy areas in the Baltic Proper (or central Baltic Sea) which is where F80 is located. However, there are indeed spatial differences in the sediment geochemistry of muddy Baltic Proper sediments. To clarify the uncertainties and limitations with our approach, the following paragraph has been added to Section 4.1: "The RTM fluxes are upscaled under the assumption that the fluxes computed for the F80 site are representative for the muddy sediment area of the Baltic Proper. This assumption is associated with uncertainties because of spatial differences in the sediment geochemistry of muddy Baltic Proper sediments as illustrated by the porewater and Fe-S chemistry for 4 other sites as published by Lenz et al. (2015). The solid phase profiles for these sites show similar temporal trends over the past decades as F80. Furthermore, the porewater profiles show that site F80 has a relatively high rate of organic matter deposition and alkalinity regeneration when compared most of the other sites. This implies that, with our extrapolation, the role of the sediment could be slightly overestimated. Thus, the large-scale fluxes we obtain by extrapolating fluxes from one specific site are to be regarded as a high-end estimate of e.g. the possible contribution of Fe-S burial to the overall TA budget".

The authors also admitted that historical TA measurement in rivers may have bias due to the lack of modern analytical standard (such as CRM) and approaches. If they can add a section of error analysis and see how that could contribute to the "missing" TA in the BALTSEM model. Given that groundwater and river could both contribute large fraction of TA budget in this area and potentially changing hydrological conditions, a

BGD

Interactive
comment

Printer-friendly version

Discussion paper



lack of this analysis make the entire argument in the manuscript a bit flawed.

Response: It is mainly the historical measurements in the Baltic Sea (and not in the rivers) that are unreliable – at least in certain periods. This is partly due to methods, and (probably more important) partly due to handling of the water samples. For example, many measurements from the 1980's and early 1990's are very likely flawed (as discussed in Section 4.4). The simulated river loads of TA are (as described in Section 2.1.3) based on measurements in the period 1996-2000 where we have data from most of the major rivers entering the Baltic. The reason that we use only this short period is that it is a major obstacle to achieve data from many of the large (and alkalinity-rich) continental rivers (whereas we have long time-series from Swedish and Finnish alkalinity-poor rivers). It is furthermore difficult to judge the quality of measurements in some of these rivers but we don't know how large the error might be and how much of the missing source that can be resolved if it were possible to reliably update the river loads. One main purpose of this paper is to estimate how much sedimentary processes can contribute to the overall TA budget of the Baltic Sea – and in particular to what extent these processes can explain the missing link. Trying to improve the river loads has not been a goal although this is something that we very much would like to do in future studies. But again, the bottleneck here is really to achieve (high-quality) data from all major rivers in the first place. Nevertheless, to clarify a bit of the uncertainty related to the parameterization of the unresolved sources, we added a second BALTSEM simulation where the unresolved sources in the various sub-basins are added as land loads instead of sediment release. Thus, the simulations now cover the two extreme cases where the unresolved source is either explained by land loads or by sediment release. We did however not want to speculate about how these contributions might vary between the different basins (see further in comment below).

I would also add a table on the types of reactions involved in both the BALTSEM and RTM models. The authors discussed them in multiple places but sometime they were rambling, which makes it hard to follow.

BGD

Interactive
comment

Printer-friendly version

Discussion paper



Response: We agree. In the current version, it may not be so easy for the reader to keep track of what is included in the different models and what is not included (without consulting prior studies). We have now added three new tables to the supplementary material: In Table S1-S2 we list primary and secondary redox reactions included in the RTM, while in Table S3 we list the TA influencing reactions included in BALTSEM. This will now also be clearly indicated in Section 2.2.1 and Section 2.2.2.

Scientific questions:

P3 L2-L8, the background on TA budget is not clear. First Gustafsson et al. stated that there is an additional TA source of 344 Gmol/yr is needed to close the Baltic Sea TA budget, and 260 Gmol/yr cannot be explained, while 84 Gmol/yr was resolved with 18 Gmol/yr was attributed to net sulfate reduction. At this point, it seems that the problem has been resolved (net sulfate reduction). Then on L7, it seems that the authors separated FeS burial from net sulfate reduction, although FeS involves net sulfate reduction. Therefore, these budgetary terms need better explanation.

Response: BALTSEM calculates the net sulfate reduction (sulfate reduction minus sulfide oxidation), but this TA source is completely reversible depending on oxygen conditions. Fe-S burial is not included in BALTSEM because we are not presently capable of modelling the coupled Fe-S cycling in the sediments (Fe is not included in the model). Thus, Fe-S burial is a TA source that we can't explicitly take into account in BALTSEM, and this is why we need the RTM where the sedimentary processes are resolved in detail. We updated the text in Section 1: "The remaining 18 Gmol y⁻¹ resulted from net sulfate reduction (sulfate reduction – sulfide oxidation) in the water column, but this fraction could be reversed in case of oxygenation of the water column. It was hypothesized that a significant fraction of the unresolved TA source could be coupled to burial of Fe sulfides as a result of anaerobic mineralization in sediments. This would then represent a fraction of the sulfate reduction that is not readily reversed upon re-oxygenation of the water column."

[Printer-friendly version](#)[Discussion paper](#)

P6 L16-30, the argument is weak. If the alkalinity contribution isn't known well (L28), how would the authors feel comfortable to run the calibration and ascertain the direction of sedimentary TA flux?

Response: As described above, we have added a second BALTSEM simulation where the unresolved sources are instead added as land loads to the different sub-basins. The following paragraph has been added to Section 2.2.2: “The processes behind the unresolved TA sources are not known, but there are two candidates: external loads (e.g. river loads and submarine groundwater discharge) and internal processes (pelagic and/or benthic). Rather than speculating about contributions from various sources in the different sub-basins, we will perform two different scenarios: one case where all unresolved sources are added as additional land loads, and one case where the sources are added as sediment release”. The resulting TA concentrations in different sub-basins are added as additional lines in Fig. 5-6, and the following paragraph is included in Section 4.2: “In the two different scenarios where the unresolved source is added as land loads (full lines in Fig. 5-6) or sediment release (dashed lines in Fig. 5-6), the simulated surface water TA concentrations are very similar (Fig. 5). Deep water concentrations on the other hand differ significantly in the Gotland Sea and the Gulf of Finland but not in the other sub-basins (Fig. 6). The reason behind the rather similar results for these two different scenarios is that land loads supplied to the different basins are rapidly distributed in the well mixed surface layer, and the well mixed surface layer constitutes a large majority of the water volume. In the deeper and more isolated parts of the system, TA concentrations are considerably lower in the “land loads” case compared to the “sediment release” case. This is a clear indication of the need for an additional TA source in the deeper basins”.

P8 L23-25, First if you refer to a multiple panel figure, please try to using letters (a, b, c...) to distinguish these panels. More importantly, if sulfide is being produced, according to reaction stoichiometry the authors presented, it would lead to TA accumulation, regardless whether this sulfide goes down or not.

Response: In the revised manuscript we will add letters to the sub-plots and corresponding parts of the text when the figure is discussed. The other point that the reviewer raises here is an excellent point. The argument on P8 L23-25 refers to the fact that the model overestimates the buildup of 2S. Indeed, the production of sulfide leads to a generation of TA if this sulfide is not reoxidized, as is the case in the current model simulation where the sulfide is being built up in the porewater (which we argue is an artefact resulting from the chosen lower boundary condition for 2S). We cannot assess the fate of the sulfide when it would diffuse downwards below 32 cm depth, as we suggest that actually happens. This makes it difficult to link this 2S production to a permanent, long-term TA source. However, we agree that it is not likely that the 2S will be reoxidized in the time period of interest. This indicates that the net TA source to the water column due to sulfide oxidation would be higher. In the revised manuscript, we will address this and quantify the additional TA generation due to the buildup of 2S in the porewater.

P9 L8-11, the statement that maximum CH₄-driven sulfate reduction at 8 cm is the greatest is interesting and need better explanation. If you show sulfate profile, this may look like where the sulfate-methane interface (SMZ) is and may have nothing to do with the temporal variations of CH₄ production.

Response: This is a valid point raised by the reviewer. The percentage of CH₄-driven sulfate reduction due to upward diffusing CH₄, which is on average ~95% for the period 1970-2009, does change over time (on average ~98, ~98, ~98 and ~94% for the four periods 1970-1973, 1973-1978, 1978-1981 and 1981-2009, respectively), but this change is indeed relatively minor, and upward diffusing CH₄ still dominates. So, we agree that the change in position of the SMTZ is more important here. The temporal evolution of porewater profiles of SO₄ and CH₄ are presented in Reed et al. (2016, their Fig. 6). From this it follows that the position of the SMTZ is shifting upwards over time, especially since 1981, when Fe(OH)₃ and O₂ declined as important terminal electron acceptors. Therefore, more SO₄ was consumed by OM degradation, and the

[Printer-friendly version](#)[Discussion paper](#)

SMTZ shifted upwards. We will address this in the revised manuscript by replacing the NH₄ and PO₄ plots in Fig. 3 by the SO₄ and CH₄ plots, adding the location of the SMTZ for the various time periods, and altering the text to include the above discussion.

P9 L12 paragraph, the authors separated different depth layers to account for the reactions that have TA implications. However, they failed to show whether TA produced in these layers make it up to TA efflux to the water column. This paragraph needs better organization and clarification.

Response: Throughout the manuscript, we argue extensively that TA effluxes are not representative for answering the research question that we are investigating (e.g. section 2.2.3, P8 L30ff, section 4.1, P15 L23ff). We therefore decided not to discuss the TA efflux in too much detail. The results discussed in the paragraph on P9 L12ff indicate, similarly to P15 L23ff, that processes that impact the TA efflux are not the same processes that impact S burial or total TA generation, but that the sediment depth at which processes take place also plays a role here. In the revised manuscript we will further stress this message.

Technical comments:

Indentation of paragraphs would be useful

Response: Indentations are now added.

P2 L20-L25, these sentences are a bit confusing. "On a system scale" is mentioned twice (L20 and L24). The two examples after "For examples" are essentially the same thing, so it's not clear why the authors used "however" to connect the two sentences.

Response: This section is now rewritten, and the paragraph reads as follows: "The ultimate buildup of TA due to primary production and mineralization depends on the source of the reactants and/or the fate of the products of all alkalinity-generating/consuming reactions. For example, production of dinitrogen gas (N₂) during pelagic or benthic denitrification results in a permanent loss of nitrate and hence a gain of TA (Soetaert

BGD

Interactive
comment

Printer-friendly version

Discussion paper



et al., 2007). On a system scale this process only results in net TA production if the nitrate is derived from an external source rather than from local nitrification (Hu and Cai, 2011b). Similarly, sulfate reduction leads to net TA generation only if the produced sulfide is buried as e.g. iron (Fe) sulfides rather than being reoxidized within the same system (Hu and Cai, 2011a). Note that the location of sulfide reoxidation, i.e. sediment or water column, impacts net TA generation in the sediments but not on a system scale”.

P3 L3, "unresolved" TA is 260 Gmol/yr, while in P9 L22 this number is 257.5 Gmol/yr, please be consistent.

Response: Corrected.

P3 L20, the two paragraphs need a better transition. Elemental sulfur seems to be introduced into the context suddenly. Prior to doing so, the authors need to explain a bit of the type of reduced sulfur burial, i.e., sulfide (with Fe) and elemental sulfur. Relative abundance of these two types of reduced sulfur also needs to be presented based on the literature.

Response: With S we indicate (reduced) solid sulfur in any form, not only elemental sulfur. For the rest, this comment ties in with the comment below, where it is suggested to move the text of P4 L6ff to the introduction. When doing so, we directly explain why for this work it is not relevant in which form the elemental sulfur is present.

P4 L1, is it integrated to 25 cm "interval"?

Response: Yes, we mean the interval between 0 and 25 cm sediment depth. This will be rewritten.

P4 L6-L15, this should go into the Introduction, as really this should be background information, by no means materials and methods.

Response: We partly agree with the reviewer here, and in the revised manuscript most of this text will be moved to the introduction. However, we are aware that various

[Printer-friendly version](#)[Discussion paper](#)

papers use various reaction equations and stoichiometries to link sulfur burial / pyrite production, mostly depending on the temporal and / or spatial scale of investigation. For example, in Łukawska-Matuszewska and Graca (2018) a different reaction equation was used for this. Therefore, we think it is important to explain the rationale behind our choice of reaction equations, and the materials and methods seems like a proper place to do so.

P4 L24, move "for that reason" to the beginning of the sentence.

Response: Ok.

P4 L25, where exactly does sigma-H₂S come from?

Response: This is now explained in Section 2.1.2 ($2S = [HS^-] + [H_2S]$).

P5 L5 paragraph, while the authors referred to a supplemental table in a published study, it would be desirable to include such information in their own supplemental materials and refer to it in the context. Otherwise the readers can easily get lost.

Response: Reactions included in the RTM and BALTSEM respectively are now described in Table S1-2 (RTM) and Table S3 (BALTSEM), respectively (see comment above).

P5 L17, not a complete sentence.

Response: We are not sure which sentence this refers to; this section seems fine.

P7 Line 12, what is "This" approach?

Response: This is now rewritten.

P7 L25 and P8 L10, why are the two sulfur burial in the same time period (1970-2009) different?

Response: Part of the sulfur solids is derived from settling of water-column particles onto the sediment surface. This cannot be derived by looking at the S solids concen-

[Printer-friendly version](#)[Discussion paper](#)

trations alone (P7 L25), but becomes clear when investigating the inputs of FeS₂ to the sediment (Figure 2) and in-situ reaction rates (Table S3; P8 L10), as is done with the RTM. For the net TA generation, however, the total S burial is most important, because the burial prevents possible re-oxidation in either sediment or water column and thus represents the long-term TA source that we are interested in.

P11 L9, where is 166 Gmol/yr in Table 5?

Response: It is there, sub-basin 7-9. The description of the division into different sub-basins and larger areas has been improved in the text. This is now described in the caption of Fig. 1 and also in the text (Section 2.1.1 and Section 4.2). The legends of Table 1 and 5 have been updated as well for clarity.

P11 L29 and P9 L 8, I believe 43% and 43.8% in these two places are the same thing, please be consistent, at least don't round off the number in the wrong way.

Response: This is correct and must have been a typo, as the correct (non-rounded) percentage is 43.3%. We will use ~43% on both occasions.

P11 Section 4.2, both unit TA (mmol/m²/yr) and overall TA flux (Gmol/yr) are presented, I'd suggest that you stick with one or both (with parentheses) to avoid confusion and don't let the readers to do the conversion.

Response: Throughout the manuscript, we stick to mmol/m²/y when discussing the sedimentary fluxes. Only when we link the results to BALTSEM, like in this paragraph, we convert them to Gmol/y.

P12 L1 and P11 L31, this sounds like freshwater environment but not typical marine since sulfate is depleted but there is still oxidized Fe.

Response: Iron-mediated anaerobic oxidation of methane has found to be significant in deeper Baltic Sea sediments that were subjected to a lake-marine transition (Egger et al., 2017), as well as in coastal sediments of the Bothnian Sea, which has low salinity (Rooze et al., 2016). Indeed, these conditions are not typical marine, so discussing

[Printer-friendly version](#)[Discussion paper](#)

this process is not too relevant in the context of this manuscript. We included it to be as complete as possible, but will remove it from the revised version of the manuscript.

P14 L6, not precise, it's the deposition of SO_x and NO_x that contribute to TA reduction, ammonia deposition first increase TA and decrease upon oxidation (or biological uptake), if no biological effect is involved, there is no TA implication, i.e., deposition followed by oxidation or uptake.

Response: Good point. This is how it is implemented in the code. The text has now been adjusted to clarify this (Section 4.6).

P14, the title of Section 4.5, this is not implications, rather simulations of future scenarios.

Response: We agree. The title has been changed to better suit the contents.

P15 L29, please update the link.

Response: Updated, and also the reference itself has been changed and now reads: van Heuven, S., Pierrot, D., Rae, J.W.B., Lewis, E. and Wallace, D.W.R.: MATLAB Program Developed for CO₂ System Calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1, 2011 to van Heuven et al. (2011).

P15 L33-34, what about including possible temperature increase? It would be a better approach to simulate future pH with invariant TA, like in most studies.

Response: The temperature increase (and also the salinity decrease) is already included in the BALTSEM simulation (approximately 3 degrees C, see Section 4.5 and Fig. S5). We did not however examine the pH sensitivity to temperature change – this is an interesting topic and the BALTSEM model would indeed be a useful tool. But, this study is primarily focused on TA dynamics; we did not want to weigh it down with further sensitivity analyses. Using invariant TA has as you say been done in prior

studies, and one main topic of this study is the effect of (long-term) changes in TA. For those reasons we did not consider scenarios with invariant TA.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2018-313/bg-2018-313-AC3-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-313>, 2018.

BGD

Interactive
comment

Printer-friendly version

Discussion paper



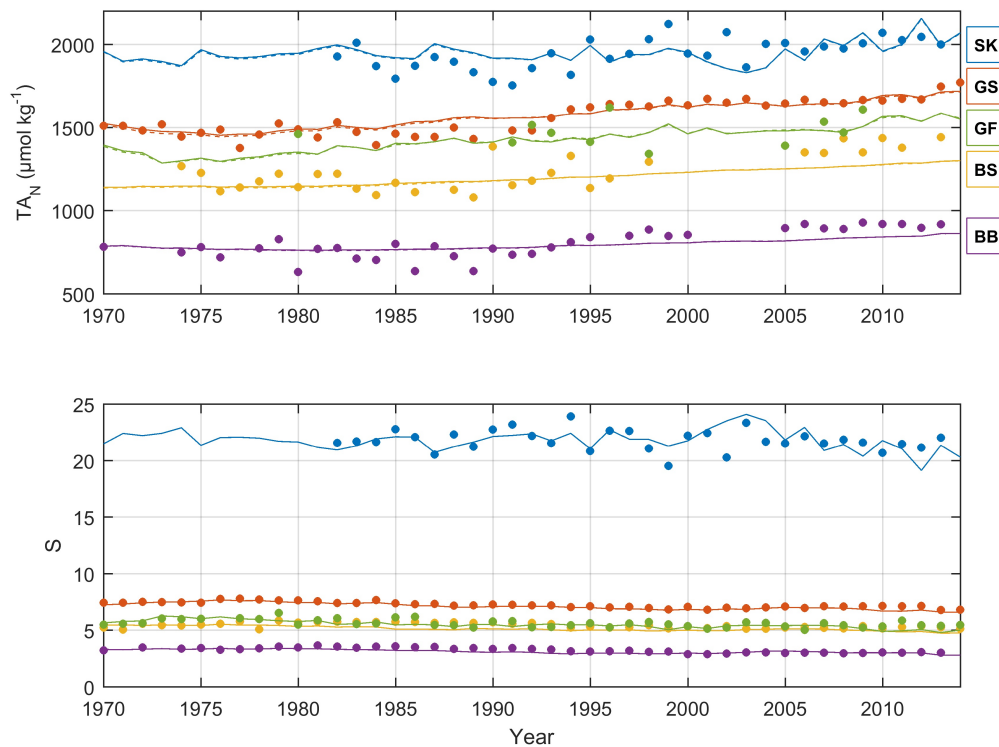


Fig. 1. New Figure 5

[Printer-friendly version](#)[Discussion paper](#)

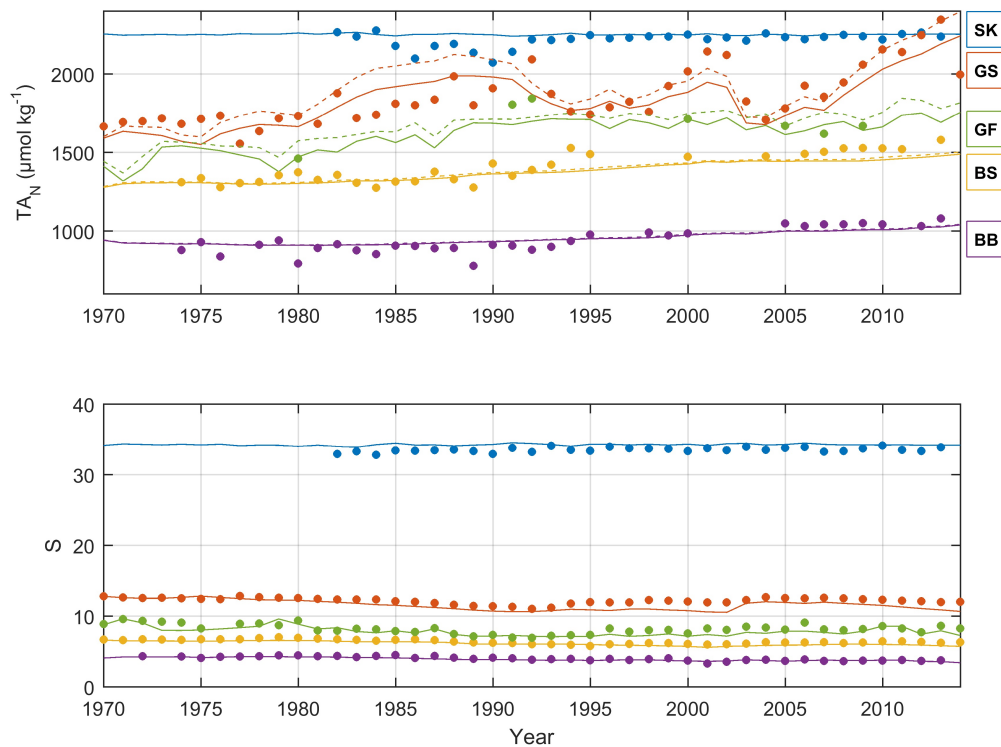


Fig. 2. New Figure 6

[Printer-friendly version](#)[Discussion paper](#)