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

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Overall Statements The manuscript "Sedimentary alkalinity generation and long-term alkalinity development in the Baltic Sea" by Erik Gustafsson and colleagues presents the simulated development of alkalinity generation in the Baltic Sea over the last decades and, additionally, projections until 2100. The modelling tools include a reactive-transport model (RTM) for sedimentary processes which is able to resolve Fe-S cycling and burial of corresponding components, which in turn generates TA. Such irreversible processes are necessary to describe the missing (unresolved) contributors to the overall TA sources in the Baltic Sea. Instead of a coupled physical – biogeochemical 3D model which couples benthic and pelagic processes, the authors use the less expensive model BALTSEM for the different Baltic Sea basins and the RTM which

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Discussion paper

is weakly coupled to BALTSEM. For the reader it is unclear which information (fluxes) are provided for RTM by BALTSEM and vice versa. A full bidirectional coupling of both models, which is claimed as not feasible (I doubt) will definitively produce results differing from the weak applied coupling. It is necessary to estimate the error induced by this weak coupling. I suggest to test this with an application of BALTSEM for one water column and the underlying RTM sediment core. Within one scenario the weak coupling should be applied and within another scenario a full coupling should run. With these two results the authors can compare the TA generation of both scenarios and hopefully are able to demonstrate that the result of the weak coupling shows the main TA-related features as the full coupled run.

Response: One main problem with the implementation of a full coupling between the two models is that the same state variables would have to be included in both models. This would in particular require a completely new version of BALTSEM that includes e.g. Fe2+, Fe(OH)3, Mn2+, MnO2, S0, FeS, FeS2, etc. For each new state variable, we would furthermore need external loads and boundary conditions. This is not impossible but a massive undertaking and not a realistic goal for the time being. Since the external loads are poorly known, this would in addition add large uncertainties. Developing a BALTSEM version with just one water column would not remove such obstacles. To clarify these obstacles, the last paragraph of Section 2.2.3 now reads: “Ideally the RTM would be dynamically coupled to BALTSEM, but this is currently not feasible for three reasons: The main reason is that the state variables used in the two models would have to match so that the same reactions can be simulated in both models. This means in particular that we would have to add several new state variables to BALTSEM (CH4, FeS, FeS2, S0, Fe2+, Mn2+, amorphous and well-crystalline Fe and Mn oxides, etc., cf. Table S1-S3). For each new state variable BALTSEM would furthermore need external loads and boundary conditions. Implementation of a full coupling between the two models is in other words a massive task and far beyond the scope of this study. Second, BALTSEM has approximately 1400 sediment “boxes”, and the RTM would have to compute the sediment processes in each of these boxes – resulting in a great computational cost. Third, calibration of the RTM in various parts of the Baltic Sea would be problematic because of an insufficient coverage of sediment data. Thus, the two models are not directly coupled to one another but instead used independently". A realistic future goal would be to develop an intermediate version of BALTSEM that includes the aspects of sedimentary Fe-S cycling that we believe to be crucial, but not the detail that is possible in the RTM. Section 4.1 has been updated with the following paragraph: "Although a full coupling between the two models is not a realistic goal at the moment, development of sediment processes in BALTSEM is decidedly a highly desirable future goal. In particular, the sedimentary Fe-S dynamics and related phosphorus cycling would serve to improve our understanding of both TA and phosphorus dynamics on a system scale. The present study can be seen as an intermediate step towards a more detailed (if not complete) description of sediment processes in the Baltic Sea. In fact, the relatively large influence of sedimentary processes on TA dynamics that we demonstrate in this study also serves as a motivation to pursue this goal". The two models are used independently which means there are no new errors induced by a weak coupling. The two models do of course have individual shortcomings and uncertainties. The RTM is used to estimate how much the sedimentary Fe-S cycling could contribute to the Baltic Sea TA budget. Results are then compared to the large-scale BALTSEM model and this exercise quantitatively demonstrates the importance of sedimentary processes compared to other (external and internal) TA sources and sinks. To clarify what processes are included in which model, we have added three new tables (Table S1- S3) where the processes and state variables included in each model are listed (this will also be clearly indicated in the model descriptions in Section 2.2.1 and 2.2.2 respectively).

One of the main conclusions of the manuscript is that Fe-S dynamics impact the TA generation only on longer time scales. This is derived from one sentence on page 15 line 23. For this conclusion I expect a deeper analysis.

Response: We do not believe that this is one of the main conclusions of the manuscript, and we are not sure how the reviewer arrived at this interpretation of the manuscript. Page 15, line 23 says: "Lowering the Fe-oxide loading to pre-1973 values decreases the S burial by an order of magnitude, confirming its limitation by Fe. Strikingly, the TA efflux is only marginally impacted, indicating the decoupling between short-term flux dynamics and long-term TA generation" What we discuss here is the mismatch between sedimentary TA generation and the modelled effluxes of TA. This topic is also discussed elsewhere in the manuscript (e.g. P9, L10-16). Instead, one of the main conclusions is that burial of Fe sulfides is a major process impacting long-term TA generation in the Baltic Sea. This indicates both different spatial and temporal scales than the reviewer's statement; one should interpret long-term TA generation as the net TA generation, i.e. the TA change occurring after all re-oxidation reactions took place, in the coupled water column-sediment system. TA generation through various processes at a specific moment in time within different zones in the sediment is highly impacted by Fe-S dynamics, as e.g. Table 4 and Figure 3 show, and as is discussed extensively in Section 3.1. We will sharpen our language in the revised manuscript in such a way that this confusion cannot arise.

Detailed remarks

P2 L3: Sarmiento and Gruber, 2006: Ref missing

Response: Corrected.

P2 L8: Rabalais et al., 2015: Ref says 2014

Response: Corrected.

P2 L17 and L25 Reference List shows only Hu and Cai, 2011

Response: No, both are there! (This is much easier to see now that indentations have been added).

P3 L1: Table 1 in Gustafsson et al 2014b gives 453 Gmol yr-1 as riverine TA load.

Response: We refer to the value used in the budget calculations (Table 3 by Gustafsson et al., 2014b). The text has been slightly adjusted to clarify this.

P4 L21: The expression $\Sigma H2S$ must be introduced.

Response: The definition ($\Sigma H2S$ = [HS-] + [H2S]) is now included in Section 2.2.1.

P5 L2: How large was the increase of TA loads when the new Swedish and Finnish data were included?

Response: As can be seen in Fig. S2 (supplementary material), the TA loads from Finnish rivers appear to be rather constant. However, we only have 10-year record for all Finnish rivers, so of course it is not easy to determine a trend. But, we also looked into 3 northern Finnish rivers that have 40-year data and found a generally increasing DIC flux to the Baltic. This concludes increasing weathering fluxes by 10-20% over the last 40 years (Sun et al., 2017, Chemical Geology). In Swedish rivers there is on average an increase of more than 5 Gmol over a 25-year period (Fig. S2). This is a significant increase compared to the total load from Swedish rivers ($\sim$40 Gmol yr-1), but compared to the TA pools in the Baltic Sea (in total $\sim$33000 Gmol; Gustafsson et al., 2014b) this is of marginal importance.

P5 L17: Lukawska-Matuszewska and Kielczewska, 2016

Response: The list of references accidentally mentioned an incorrect paper. It should have said: Łukawska-Matuszewska, K.: Contribution of non-carbonate inorganic and organic alkalinity to total measured alkalinity in pore waters in marine sediments (Gulf of Gdansk, S-E Baltic Sea), Marine Chemistry, 186, 211–220, doi:10.1016/j.marchem.2016.10.002, 2016. This is now corrected.

P6 L18: The use of these unresolved fluxes is very unsatisfying. They might also represent sinks that are assumed too high. Using such a “joker”, it’s relatively easy to match observed TA concentrations.

Response: Yes, the unresolved fluxes could include overestimated sinks (probably a minor part though). The purpose of the simulated unresolved fluxes was to match observed TA concentrations as closely as possible and further to close the TA budget of the Baltic Sea.

P7 L3ff: How do you handle the lateral Fe input? How do you treat S burial and the consecutive TA flux into the pelagic? The normal way across pore water diffusion in connection with overlying water cannot work with this model setup.

Response: Variations in the lateral input of Fe have been described as variations in the amount and form of Fe deposited onto the sediment, as shown in Figure 2. The paper by Reed et al. (2016) provides more details on the choices of this; as the manuscript is already quite long as is, and the model calibration did not make up part of this work, we did not want to repeat too many of the details. Instead, we now included additional references to either Figure 2 or the work of Reed et al. (2016) in the manuscript where necessary. The point the reviewer makes here is one of the reasons why we do not directly link calculated effluxes to changes in the water column. Instead, the amount of S burial in a specific year is assumed to represent a release of TA from the sediments within that year. Given the relatively long time scale that we are looking at (averages over multiple years) compared to the actual rate of formation, we can assume that all TA associated with S burial will have diffused upwards and escaped the sediment. This is already briefly indicated in Section 3, but will be discussed more explicitly in section 2.2.3 as well.

P7 L10 Describe the upscaling process in more detail.

Response: After translating S burial to an efflux of TA (see response to previous comment), with units of mmol TA m-2 y-1, we assumed this flux to be representative for the entire muddy area of the Baltic Proper. This is further detailed in Section 4.2, but it is now also specified in Section 2.2.3 where the first paragraph is extended as follows: "...The RTM on the other hand resolves these processes in detail and quantifies the fluxes at specific sites. At present, it is not feasible to upscale such site-specific fluxes to the system-scale – in the present study fluxes computed by the RTM are instead upscaled to cover a certain bottom type in the relevant sub-basin (i.e., the total muddy sediment area). This was done by multiplying the TA efflux (mmol m-2 y-1) by the muddy sediment area of the Baltic Proper (Table 1)".

P7 L19 I do not see the problem to handle 1400 sediment "boxes".

Response: In Section 2.2.3 we have now clarified the main bottlenecks related to a full coupling of the models. Handling 1400 sediment boxes is one of those, but certainly not the most important one. See reply above.

P7 L22 You should say that the current model setup is only an intermediate step towards full coupling.

Response: A full coupling is probably not a realistic goal for the time being for reasons described in Section 2.2.3 (see comment above). However, an improved description of sediment dynamics in BALTSEM is a highly desirable future goal. A new paragraph discussing future goals has been added to Section 4.1 (see comment above).

P10 L14-20 The text is non-transparent. Enumerate all shortcuts and discuss their implications. Specify the processes and species, which cannot be linked. Here, the above mentioned sensitivity study should be discussed.

Response: The text in Section 4.1 has now been updated with references to our new Tables S1-S3 as well as to the updated Section 2.2.3 (described in comment above): "BALTSEM includes many biogeochemical processes that produce and consume TA both reversibly and irreversibly on short time scales and in many boxes within each sub-basin of the Baltic Sea. These processes are described in Section 2.2.2 and are further listed in detail in Table S3. BALTSEM furthermore accounts for land loads, atmospheric depositions, and TA exchange between sub-basins and between the Baltic Sea and the North Sea. The result of the model simulations, i.e. the long-term development of TA in various sub-basins, is what we compare to observations in the water

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Discussion paper

column (Fig. 5-6). Similarly, the RTM calculates net TA generation due to various reversible and irreversible processes (described in detail in Table S1-S2). If we dynamically coupled the RTM to BALTSEM, we would have to consider all these processes, and link all species between both models. Given the unfeasibility of this, as discussed in Section 2.2.3, we couple both models by using the output of the RTM to further constrain BALTSEM. Specifically, we explain part of the source of BALTSEM that is unresolved but necessary to describe the long-term TA development in the Baltic Sea".

P12 L24 Dijkstra et al,. 2018: Ref says 2017

Response: The reference has been updated and now reads: Dijkstra, N., Hagens, M., Egger, M. and Slomp, C. P.: Post-depositional formation of vivianite-type minerals alters sediment phosphorus records, Biogeosciences, 15(3), 861–883, doi:https://doi.org/10.5194/bg-15-861-2018, 2018.

P15 L23: "Striking .." Discuss this item in more detail. Why would you have assumed a stronger impact? Which mechanism hampers it?

Response: We agree this is an interesting finding that warrants a further explanation. If we had assumed a tight coupling between S burial and modelled TA effluxes, we would have expected a decline in TA efflux as well. However, averaged over the 41-year period, we do not observe this at all, while we expected to see at least some response in the modelled TA effluxes. In part, this can be because in this scenario the amount of TA generation due to OM degradation (2855 mmol m-2 y-1) exceeds by far the amount of TA generation due to S burial (46 mmol m-2 y-1), also under business-as-usual (470 mmol m-2 y-1). Also, because an important source of reduced S comes from below, due to SO4-AOM at depth, the formation of S solids generally occurs deeper in the sediment than OM degradation. In contrast, we did see a strong decline in modelled TA effluxes when the OM loading is lowered. This suggests that the modelled TA effluxes are indeed dominated by the amount of OM degradation. On P9, L12ff we already discussed the interesting link between modelled TA efflux and changes in iron loading, and how the depth at which reactions occur is also relevant for the modelled TA efflux. We will further stress this message in the revised manuscript. We already discussed earlier in the manuscript that we cannot directly use modelled TA effluxes to study the effect on long-term TA development (P8 L.30ff). The modelled TA efflux is a combined effect of many TA generating (and consuming) processes occurring in the sediment. As such, it 'blurs' the signal of S burial. Most of these sedimentary TA generating (and consuming) processes are compensated for in the water column on the time scale that we are interested in, such that only the burial of S remains as the relevant process on the long term.

P19 L6: "2014a"

Response: Corrected.

P19 L9: "2014b"

Response: Corrected.

P36 L3: Ruppin (1909): Ref missing

Response: Corrected.

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