Authors' response

A 'track changes'-version of the manuscript is included after the point-by-point responses.

Response to referee #1

Page and line numbers in the responses below refer to the 'track changes'-version of the manuscript.

This manuscript reports alkalinity development in the Baltic Sea since 1970 based on two models. I am, however, not convinced about the results as there is a lot of extrapolation, and the calculations are done without an error analysis. For instance, it is said that 260 Gmol/y of the additional TA source can not be explained but there is no error bar. In fact, most of the numbers given have no error bars.

Response: The standard deviation of all terms in the TA budget has now been added in Table 5 and also in the text (Section 3.2, P11 L13-14).

My other major concerns are: 1. Sulfur in umol/g is converted to umol/cm3 using measured porosity but this can not be done using porosity alone.

Response: Besides porosity, a sediment density of 2.65 g cm^{-3} *is used for this conversion, which is typical for marine sediments. This is now added in the manuscript (Section 2.1.1, P4 L6).*

2. The results are integrated to 25cm and extrapolated to basin scale. But, how reliable is the age model and how homogeneous is the sediments in the Baltic Sea? I would expect a lot of variability in both but the uncertainty is not evaluated.

Response: The age model for site F80 is extensively discussed by Lenz et al. (2015b). Briefly, it was constructed using high-resolution Mo and Mn data obtained by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) line scanning. By comparing fluctuations in Mo/Al and Mn/Al with instrumental records of bottom water oxygen conditions, ages were assigned to features in these profiles. It is the best age model available for this site, and as already shown by Reed et al. (2016), matches well with likely scenarios regarding bottom-water oxygenation and organic matter input. Assuming that the upper 25 cm of the sediment represents the period 1970-2009, is thus validated, in our opinion.

As also responded to Reviewer 3, we would like to stress that we extrapolate our results not over the entire Baltic Sea, but only over muddy sediments 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 (P13 L1-8):

"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 pore water 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 pore water profiles show that site F80 has a relatively high rate of organic matter deposition and alkalinity regeneration when compared to 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 maximum estimate of the contribution of S burial to the overall TA budget of up to 26%".

3. It is said that borate is ignored because it is expected to have a low contribution to TA. I am surprised. What is the basis for such a statement?

Response: Borate is included in BALTSEM as indicated in the new Equation 4 (P6 L19-20) as well as in the supplementary material; the contribution in most areas is small because of the low salinity, although one exception is the entrance area with more oceanic conditions. In the RTM on the other hand, borate is not included as its contribution to TA is even smaller. With S=12 (i.e. total boron = 142.5 umol/kg according to Uppström, 1974) and prevailing conditions, bottom-water borate alkalinity (BA) is ~9e-3 mM, while measured TA equals 2.2 mM. Thus, BA contributes only 0.4% to TA in the bottom-water. With no significant source or sink term for boron in the sediments, its contribution to TA sharply declines with sediment depth. It is thus acceptable to ignore this term in the RTM.

My minor concern is the statement that the Baltic Sea today forms the largest anthropogenic dead zone is the world. It is not true. There are many dead zones in the Baltic Sea so the authors must have summed them up. If one sums up separate dead zones in other seas, such as the East China Sea, the total area is much larger. In fact, the dead zone off the Changjiang river mouth alone is now larger.

Response: We now write "one of the largest" instead of "the largest" (Section 1, P2 L33).

Response to referee #2

Page and line numbers in the responses below refer to the 'track changes'-version of the manuscript.

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 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. Fe^{2+}, $Fe(OH)_3$, Mn^{2+}, MnO_2, S_0, FeS, FeS_2, *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 issues, the last paragraph of Section 2.2.3 (P8 L19-27) now reads: "Ideally the RTM would be dynamically coupled to BALTSEM, but this is currently not feasible for two reasons: First and foremost, direct coupling would require 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 that we would have to add numerous new state variables to BALTSEM (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 – calibration of the RTM in various parts of the Baltic Sea would be problematic *because of an insufficient coverage of sediment data. Therefore, 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 (P13 L9-14) has been updated with the following paragraph: "Although a full coupling between the two models is not a realistic goal at the moment, the development of sediment processes in BALTSEM is decidedly a highly desirable future goal. In particular, the inclusion of sedimentary Fe-S dynamics and related phosphorus (P) cycling would serve to improve our understanding of both TA and P dynamics on a system scale. The present study can be seen as an intermediate step towards a more detailed (if not complete) model 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 is also 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. P18 L22-24 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 again the decoupling between short-term flux dynamics and long-term TA generation, as discussed extensively in Sections 2.2.3 and 3.1" What we discuss here is the mismatch between sedimentary TA generation and the modelled effluxes of TA.

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 have sharpened 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 ΣH2S must be introduced.

Response: The definition ($\Sigma H_2S = [HS^-] + [H_2S]$) *is now included in Section 1, P3 L8.*

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 (~40 Gmol yr^{-1}*), but compared to the TA pools in the Baltic Sea (in total ~33000 Gmol; Gustafsson et al., 2014b) this is of marginal importance.*

Reference: Sun, X., Mörth, C.-M., Humborg, C. and Gustafsson, B.: Temporal and spatial variations of rock weathering and CO2 consumption in the Baltic Sea catchment, Chemical Geology, 466, 57–69, doi:10.1016/j.chemgeo.2017.04.028, 2017.

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 discussed in Sections 2.2.3 and 3.1.

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 (P7 L30 -P8 L10) 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. It is not feasible to upscale such site-specific fluxes to the system-scale. Moreover, it would require that the fate of all components contributing to the TA efflux calculated by the RTM should be evaluated in BALTSEM. We know that a substantial part of the TA efflux from the sediment is due to components that are reoxidized in the water column. Only a full coupling between both models, which is currently not feasible as discussed below, would allow monitoring the fate of these components. We therefore use only that part of the TA efflux that is due to a sedimentary source that is permanent on the time scale of interest, i.e. the burial of reduced S. In the present study, 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 TA flux due to S burial and computed by the RTM was subsequently 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 net TA generation resulting from S burial (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 (P8 L20-27) 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 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 (P12 L7-15) 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 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* SO_4*-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 L33ff 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 already discussed earlier in the manuscript that we cannot directly use modelled TA effluxes to study the effect on long-term TA development (P9 L14ff). 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.

Response to referee #3

Page and line numbers in the responses below refer to the 'track changes'-version of the manuscript.

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 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 (P13 L1-8):

"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 pore water 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 pore water profiles show that site F80 has a relatively high rate of organic matter deposition and alkalinity regeneration when compared to 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 maximum estimate of the contribution of S burial to the overall TA budget of up to 26%".

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 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 we believe 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 form 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.

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 is now also 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 cannot 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, P3 L7-9:

"The remaining 18 Gmol y^{-1} *resulted from net* SO_4^{2-} *reduction (*SO_4^{2-} *reduction – dissolved sulfide (*$\Sigma H_2S = [HS^-] + [H_2S]$*) 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* SO_4^{2-} *reduction that is not readily reversed through* ΣH_2S *oxidation upon re-oxygenation of the water column".*

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, P7 L11-17:

"The processes behind the unresolved TA source 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). In theory, the source could be associated both with processes that are not included in the model (e.g. Fe-S cycling, submarine groundwater discharge) and with processes that are included but possibly not correct (e.g. river loads, nutrient cycling). Instead of speculating about contributions from various sources in the different sub-basins, we will perform two different scenarios: one case where the unresolved source is added as additional land loads, and one case were the source is added as sediment release. The magnitudes of unresolved sources in different sub-basins are identical in the two cases".

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, P13 L24-30:

"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 lower in the "land loads" case compared to the "sediment release" case".

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 have added 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 refers to the fact that the model overestimates the buildup of $\sum H_2S$*. 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* $\sum H_2S$*). 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* $\sum H_2S$ *production to a permanent, long-term TA source. However, we agree that it is not likely that the* $\sum H_2S$ *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 address this on P9 L23-30.*

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 CH_4*-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* CH_4 *still dominates. So, we agree that the change in position of the SMTZ is more important here. The temporal evolution of porewater profiles of* SO_4 *and* CH_4 *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* O_2 *declined as important terminal electron acceptors. Therefore, more* SO_4 *was consumed by OM degradation, and the 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, 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, 3.1, 4.1). We therefore decided not to discuss the TA efflux in too much detail. We discussed 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.

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 (P2 L21-29):

"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 (N_2) during pelagic or benthic denitrification results in a permanent loss of nitrate (NO_3^-) and hence a gain of TA (Soetaert et al., 2007). On a system scale this process only results in net TA production if the NO_3^- is derived from an external source rather than from local nitrification (Hu and Cai, 2011b). Similarly, SO_4^{2-} reduction leads to net TA generation only if the produced sulfide is buried as e.g. 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 is now rewritten (P4 L7).

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, however, we are aware that various 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 1, P3 L8 ($\Sigma H_2S = [HS^-] + [H_2S]$).

P5 L5 paragraph, while the authors referred to a supplemental tablein 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 concentrations alone (P8 L30), but becomes clear when investigating the inputs of FeS_2 to the sediment (Figure 2) and in-situ reaction rates (Table S6), 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 this process is not too relevant in the context of this manuscript. We included it to be as complete as possible..

P14 L6, not precise, it's the deposition of SOx and NOx 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 4.4, P17 L5-10).

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 CO_2 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 carbonate system 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.

Sedimentary alkalinity generation and long-term alkalinity development in the Baltic Sea

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Abstract. Enhanced release of alkalinity from the seafloor, principally driven by anaerobic degradation of organic matter under low-oxygen conditions and associated secondary redox reactions, can increase the carbon dioxide (CO_2) buffering capacity of seawater and therefore oceanic CO_2 uptake. The Baltic Sea has undergone severe changes in oxygenation state and total alkalinity (TA) over the past decades. The link between these concurrent changes has not yet been investigated in detail. A recent system-wide TA budget constructed for the past 50 years using BALTSEM, a coupled physical-biogeochemical model for the whole Baltic Sea area, revealed an unknown TA source. Here we use BALTSEM in combination with observational data and one-dimensional reactive transport modelling of sedimentary processes in the Fårö Deep, a deep Baltic Sea basin, to test whether sulfate (SO_4^{2-}) reduction coupled to iron (Fe) sulfide burial can explain the missing TA source in the Baltic Proper. We calculated that this burial can account for up to 26% of the missing source in this basin, with the remaining TA possibly originating from unknown river inputs or submarine groundwater discharge. We also show that temporal variability in the input of Fe to the sediments since the 1970s drives changes in sulfur (S) burial in the Fårö Deep, suggesting that Fe availability is the ultimate limiting factor for TA generation under anoxic conditions. The implementation of projected climate change and two nutrient load scenarios for the 21st century in BALTSEM shows that reducing nutrient loads will improve deep water oxygen conditions, but at the expense of lower surface water TA concentrations, CO_2 buffering capacities and faster acidification. When these changes additionally lead to a decrease in Fe inputs to the sediment of the deep basins, anaerobic TA generation will be reduced even further, thus exacerbating acidification. This work highlights that Fe dynamics plays a key role in the release of TA from sediments where Fe sulfide formation is limited by Fe availability, as exemplified for the Baltic Sea. Moreover, it demonstrates that burial of Fe sulfides should be included in TA budgets of low oxygen basins.

1 Introduction

Assimilation of CO_2 by autotrophs followed by sedimentation and burial of organic carbon is a sink for atmospheric CO_2 (Sarmiento and Gruber, 2006). Large proportions of global oceanic primary production, organic matter burial, and sedimentary mineralization occur in coastal seas (Gattuso et al., 1998). Despite covering only ca. 7% of the oceanic surface area, coastal seas contribute ca. 10 to 20% of the global oceanic CO_2 uptake (Gattuso et al., 1998; Bauer et al., 2013; Regnier et al., 2013). One effect of eutrophication, the increased supply of organic matter to an ecosystem, is that CO_2 assimilation as well as burial of carbon (C) is enhanced (Andersson et al., 2006; Middelburg and Levin, 2009). In addition, eutrophication drives an accelerated deep water deoxygenation in many coastal systems (Diaz and Rosenberg, 2008; Rabalais et al., ~~2015~~2014; Breitburg et al., 2018). Because increased mineralization of organic matter leads to enhanced CO_2 release, eutrophication-induced hypoxia may intensify acidification in sub-surface waters of such coastal systems (Cai et al., 2011, 2017; Hagens et al., 2015; Laurent et al., 2018).

Enhanced deep water oxygen consumption may also increase the proportion of organic matter that is degraded anaerobically in both sediments and deep water. Many anaerobic degradation processes produce ~~total alkalinity (~~TA~~)~~ (Chen and Wang, 1999), which can temporarily or permanently boost the pelagic CO_2 buffering capacity and thus potentially increase the absorption of atmospheric CO_2 (or reduce CO_2 outgassing). Estimates of TA release from coastal sediments have been based both on model calculations and direct measurements, but the reported fluxes vary quite considerably depending on the methods used, processes included, and spatial and temporal scales considered (Chen, 2002; Wallmann et al., 2008; Thomas et al., 2009; Hu and Cai, 2011a; Krumins et al., 2013; Gustafsson et al., 2014b; Brenner et al., 2016).

Depending on the nitrogen (N) source, primary production can either be a source, a sink, or neutral with respect to TA (Wolf-Gladrow et al., 2007). Aerobic mineralization including nitrification of the produced ammonium (NH_4^+) is a TA sink, while anaerobic mineralization processes in general produce TA (e.g. Brenner et al., 2016). ~~On a system scale, however, t~~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 (N_2) during pelagic or benthic denitrification results in a permanent loss of nitrate (NO_3^-) and hence a gain of TA (Soetaert et al., 2007). On a system scale ~~T~~this process only results in net TA production ~~on a system scale, however,~~ if the NO_3^-~~nitrate~~ is derived from an external source rather than from local nitrification (Hu and Cai, 2011b). Similarly, SO_4^{2-}~~sulfate~~ reduction leads to net TA generation only if the produced sulfide is buried as e.g. ~~iron (Fe)~~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.

The Baltic Sea (Fig. 1) is one of many coastal seas around the globe where eutrophication has led to massive changes in both nutrient cycling and oxygen concentrations (e.g. Gustafsson et al., 2012). During the first half of the 20th century, hypoxic and anoxic conditions occurred only sporadically and affected limited deep water areas (Carstensen et al., 2014). Since the 1950s, oxygen poor areas in the Baltic Sea have expanded rapidly and today form one of the largest anthropogenic ‘dead zones’ in the world (Diaz and Rosenberg, 2008). This expansion may have led to an increase in net TA generation through anaerobic processes.

Based on available observations, ~~P~~present-day riverine TA loads to the Baltic Sea amount to ~470 Gmol y^{-1} ~~according to available observations~~ (Gustafsson et al., 2014b, their Table 3). ~~Based on~~Using budget calculations, Gustafsson et al. (2014b) estimated that an additional TA source of 344 Gmol y^{-1} is necessary to close the Baltic Sea TA budget. Approximately 260 Gmol y^{-1} of this source cannot be explained so far. Of the 84 Gmol y^{-1} that was resolved, 66 Gmol y^{-1} resulted from the net effect of primary production, aerobic mineralization, and denitrification – essentially N cycling. The remaining 18 Gmol y^{-1} resulted from net SO_4^{2-} ~~sulfate~~ reduction (SO_4^{2-} ~~sulfate~~ reduction – dissolved sulfide ($\Sigma H_2S = [HS^-] + [H_2S]$)~~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 SO_4^{2-} reduction that is not readily reversed through ΣH_2S~~sulfide~~ oxidation ~~-~~upon re-oxygenation of the water column. Due to incomplete descriptions of benthic processes in the model that was used, this hypothesis could not be tested (Gustafsson et al., 2014b), but the process has recently been identified as an important TA source in the Gdańsk Deep (Lukawska-Matuszewska and Graca, 2018).

The amount and form of Fe solids entering the sediment is a key factor controlling net benthic TA generation from Fe sulfide burial. Recent work on Fe dynamics in deep Baltic Sea basins has shown that the lateral transfer (“shuttling”) of Fe from shelves to deep basins is most intense when bottom water hypoxia is intermittent (Lenz et al, 2015a). Under such conditions, dissolved Fe can escape from the shelves, rather than being retained in the sediment as Fe oxides (in case of oxic bottom water conditions) or Fe sulfides (in case of widespread anoxia/euxinia). This Fe is then transported laterally to the deep basins, where local redox conditions determine its fate. The present-day low oxygen concentrations in many deep basins of the Baltic Sea promote SO_4^{2-} ~~sulfate~~ reduction (Reed et al., 2016), indicating enhanced net benthic TA generation due to S ~~sulfur (S)~~ burial as the escaped Fe reaches these basins. Sediment records of S concentrations can be used to calculate S burial and thus quantify the TA source associated with this burial.

Here, we use burial rates of solid phase S from the literature (Lenz et al. 2015b) and results from two different types of biogeochemical models to 1. Constrain the present-day sedimentary TA release from Baltic Sea sediments to the water column; 2. Quantify the large-scale changes in sedimentary TA release coupled to changes in eutrophication and oxygen conditions; 3. Quantify the relative influence of different processes that contribute to the sedimentary TA release and 4. Estimate the potential future development of TA and pH levels upon recovery from eutrophication and assuming continued eutrophication. The models employed in this study are a high-resolution reactive-transport sediment model (RTM) (Reed et al. 2016) and a long-term, large-scale coupled physical-biogeochemical model for the Baltic Sea, BALTSEM (Gustafsson et al., 2017).

2 Material and methods

2.1 Data

2.1.1 Sediment data and calculations

Sedimentary alkalinity generation due to S burial in the Baltic Proper (sub-basin 7-9 in Fig. 1) was estimated using published data of S contents at F80, a 191 m deep site in the Fårö Deep of the Gotland Sea (Fig. 1; Lenz et al., 2015b). Concentrations of S in µmol g^{-1} were first converted to units of µmol cm^{-3} using measured porosities and a sediment density of 2.65 g cm^{-3}~~.~~, which is typical for such sediments, and were subsequently depth-integrated between 0 and~~to~~ 25 cm sediment depth. Following the age model presented by Lenz et al. (2015b), this depth interval represents the burial since 1970, allowing the calculation of an annually averaged rate of S burial (mmol m^{-2} y^{-1}). Using a 1:2 ratio between S burial and TA generation, the latter was calculated and subsequently extrapolated to the basin scale using the total muddy sediment area for the Baltic Proper (Table 1; Al-Hamdani and Reker, 2007).

Although total S concentrations do not indicate in which form S is buried, this does not matter for the associated TA generation. The conversion from ~~sulfate (~~SO_4^{2-}~~)~~ to reduced sulfur produces 2 moles of TA (in the form of HCO_3^-) per mole of S (Eq. 1, CH_2O represents simplified organic matter). This is irrespective of whether it ultimately ends up in the form of Fe monosulfides (FeS), pyrite (FeS_2) or elemental sulfur (S^0) when being converted to a solid form. Reductive dissolution of Fe oxides also produces 2 moles of TA (as HCO_3^-) per mole of dissolved iron (Fe^{2+}) formed, but this is compensated for when Fe^{2+} subsequently reacts with dihydrogen sulfide (H_2S) during FeS formation, thereby releasing protons (Eq. 2). Therefore, there is no net TA generation associated with the formation of Fe^{2+} and its subsequent burial as Fe sulfide minerals (Hu and Cai, 2011a).

$$2CH_2O + SO_4^{=} \longrightarrow 2HCO_3^- + H_2S \qquad (1)$$

$$\tfrac{1}{4}CH_2O + Fe(OH)_3 + H_2S + \tfrac{7}{4}CO_2 \longrightarrow FeS + \tfrac{3}{4}H_2O + 2HCO_3^- + 2H^+ \qquad (2)$$

2.1.2 Oceanographic data

Measured TA and salinity in the 1970-2014 period were extracted from the ICES oceanographic database (ICES Data Set on Ocean Hydrography, the International Council for the Exploration of the Sea, Copenhagen, http://ocean.ices.dk/Helcom/) and the Swedish Ocean Archive (SHARK) database provided by the Swedish Meteorological and Hydrological Institute (SMHI; http://sharkweb.smhi.se/).

During the Swedish monitoring cruises water samples were at least occasionally stored in glass bottles with a head space of air until later analysis in the laboratory. This means that the ΣH_2S in the samples may have been oxidized by the time of analysis (cf. Ulfsbo et al., 2011), which then implies that the reported TA concentrations in anoxic water can be substantially underestimated. For that reason, ~~F~~following Ulfsbo et al. (2011) we have ~~for that reason~~ adjusted the measured TA concentrations in euxinic waters by adding the ΣH_2S concentration multiplied by a factor two (i.e., $TA_{adjusted} = TA_{observed} + 2\ \Sigma H_2S_{observed}$). However, if the ΣH_2S~~hydrogen sulfide~~ was not removed by the time of analysis, the adjusted TA concentration will be too high.

2.1.3 River data

Riverine TA concentrations in the BALTSEM model were based on monthly measurements in 1996-2000 from 82 of the major rivers entering the Baltic Sea, representing approximately 85% of the total runoff (cf. Gustafsson et al., 2014b). In this study we also include measurements from Swedish and Finnish rivers for the periods 1985-2012 and 2001-2012, respectively. Swedish chemical data were provided by the Swedish University of Agricultural Sciences (SLU; http://www.slu.se/en/), Swedish runoff data were provided by the SMHI (http://vattenwebb.smhi.se/). Finnish data were extracted from the database Hertta provided by the Finnish Environment Institute (SYKE).

2.2 Model calculations

2.2.1 Sediment reactive-transport model (RTM)

A one-dimensional reactive-transport model (Reed et al., 2016) was used to calculate benthic TA generation and release at F80, with a minor modification: the redox reaction equations as presented in Table S8 by Reed et al. (2016) were updated to include the total concentrations of the ammonium and sulfide acid-base systems, instead of the respective corresponding acid-base species. The model calculates acid-base speciation using the Direct Substitution Approach (Hofmann et al., 2008), where pH and total quantities (i.e., dissolved inorganic carbon (DIC), ΣH_2S, total ammonium ($\Sigma NH_4^+ = [NH_4^+] + [NH_3]$), etc.) are used as state variables, meaning that TA is calculated as output variable. Effluxes of TA from the sediment were subsequently calculated from the gradient in the diffusive boundary layer (Boudreau, 1997). The model includes the carbonate, sulfide, ammonium, and phosphate acid-base systems, such that TA is defined as:

$$TA = [HCO_3^-] + 2[CO_3^=] + [HPO_4^=] + 2[PO_4^{3-}] + [NH_3] + [HS^-] - [H^+] \qquad (3)$$

The RTM thus ignores contributions of the fluoride, borate and silicate acid-base systems, as well as the hydroxide ion and phosphoric acid, which make up part of the classical definition of TA (Dickson, 1981) but were expected to have a low contribution to TA in this setting. Moreover, the model neglects organic alkalinity, which can substantially contribute to Baltic Sea pore water TA (Lukawska-Matuszewska, 2016; Lukawska-Matuszewska et al., 2018), but which is challenging to calculate due to the variety of acid-base groups associated with organic matter. Further details on the governing equations, redox and equilibrium reactions, reaction parameters and boundary conditions are given in ~~Eq. S1-S22 and~~ Table S1-S2 and S4 (supplementary material), and in Reed et al. (2016).

The RTM has previously been used at this location to assess the impact of shelf-to-basin Fe ~~iron~~ shuttling on the formation and stability of the Fe(II)-phosphate mineral vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$; Reed et al., 2016). To this end, it was calibrated against a wide selection of pore water and solid phase data presented in Jilbert and Slomp (2013), Lenz et al. (2015b) and Reed et al. (2016). We confirm this calibration for the carbonate system with additional DIC and TA pore water data from a multicore recovered at F80 during a research cruise with R/V Pelagia in June 2016. Core handling and pore water analyses have been performed following Egger et al. (2016). We used the previous calibration and perform sensitivity analyses to identify the key mechanisms responsible for benthic TA generation and release. To represent the variety of bottom water conditions at site F80 since the 1970s, four time intervals were recognized (Fig. 2): 1970-1973 (baseline; I), 1973-1978 (start of change in Fe loading; II), 1978-1981 (eutrophication but pre-euxinia; III) and 1981-2009 (eutrophication and euxinia, IV).

2.2.2 Large scale physical-biogeochemical model

BALTSEM is a coupled physical-biogeochemical model developed for the Baltic Sea. The model divides the system into thirteen connected sub-basins (Fig. 1), where each basin is described as horizontally homogeneous although with a high vertical resolution and a depth dependent area distribution based on the real hypsography of the various sub-basins. A hydrodynamic module simulates mixing and advection (Gustafsson, 2000; 2003), while the dynamics of nutrients and plankton (Gustafsson et al., 2012; Savchuk et al., 2012; Gustafsson et al., 2017) as well as organic carbon and the carbonate system processes (Gustafsson et al., 2014a, b; 2015) are simulated in a coupled biogeochemical module. ~~The BALTSEM model runs cover the period 1970-2014 in the present study.~~The hindcast model simulations cover the period 1970-2014, while the scenario runs (Section 4.5) cover the period 1970-2099.

In BALTSEM, TA is based on Dickson (1981) but also includes the influence from organic alkalinity in the water column based on Kuliński et al. (2014) and Ulfsbo et al. (2015) (cf. Gustafsson et al., 2015):

$$TA = [HCO_3^-] + 2[CO_3^=] + [B(OH)_4^-] + [HPO_4^=] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] - [H^+] - [HF] - [H_3PO_4] + organic\ alkalinity \qquad (4)$$

Most biogeochemical processes related to production and mineralization in the water column and sediments either produce or consume TA. Many of these TA sources and sinks have been described in detail by e.g. Wolf-Gladrow et al. (2007) and Krumins et al. (2013) respectively. TA production/consumption resulting from processes such as ammonium/nitrate-based production, nitrification, denitrification, SO_4^{2-}~~sulfate~~ reduction, and ΣH_2S~~sulfide~~ oxidation are included in the BALTSEM calculations (Gustafsson et al., 2014b). All biogeochemical reactions that produce or consume TA in BALTSEM are given in Table S3 (supplementary material). Under euxinic conditions in the water column, SO_4^{2-}~~sulfate~~ reduction and also NH_4^+~~ammonium~~ accumulation represent large TA sources, these are however reversed if the water is again oxygenated by deep water inflows and vertical mixing. BALTSEM does not include Fe cycling, and in particular there are no parameterizations for Fe shuttling and subsequent burial of Fe sulfides in the sediments.

As mentioned in the introduction, observed river loads of TA are not sufficient to reproduce observed TA in the Baltic Sea. The additional source that is required can partly be explained by biogeochemical processes but is as yet largely unknown. This “unresolved source” was calibrated by Gustafsson et al. (2014b), and although the magnitude is well constrained, it has as yet not been possible to determine what the source is. ~~Other TA sources than river loads are, as mentioned in the introduction,~~

~~necessary to reproduce observed TA in the Baltic Sea. The additional sources can partly be explained by biogeochemical processes but are as yet largely unknown. These "unresolved sources" were calibrated by Gustafsson et al. (2014b), and although the magnitude of the unresolved source is well constrained, it has as yet not been possible to determine what this source is. In theory the source could be associated both with processes that are not included in the model (e.g. Fe-S cycling, submarine groundwater discharge, etc.) and with processes that are included but possibly not correct (e.g. river loads, nutrient cycling).~~ The BALTSEM model has since been updated both with new processes and with new forcing files. The model now includes ~~the influence from organic alkalinity in the water column based on Kuliński et al. (2014) and Ulfsbo et al. (2015) (cf. Gustafsson et al., 2015), as well as~~ the influence from acidic depositions based on Claremar et al. (2013). Furthermore, the forcing files now cover the period 1970-2014. As a result of these updates, the calibrated unresolved TA sources have been slightly modified in the present study compared to those by Gustafsson et al. (2014b) (see Section 3.2).

The processes behind the unresolved TA source 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). In theory, the source could be associated both with processes that are not included in the model (e.g. Fe-S cycling, submarine groundwater discharge) and with processes that are included but possibly not correct (e.g. river loads, nutrient cycling). Instead of speculating about contributions from various sources in the different sub-basins, we will perform two different scenarios: one case where the unresolved source is added as additional land loads, and one case were the source is added as sediment release. The magnitudes of unresolved sources in different sub-basins are identical in the two cases.

~~Although the processes behind the unresolved TA source are not known, the calibrated sources in the different sub-basins are tentatively added as a flux from the sediment to the water column.~~ Following Gustafsson et al. (2014b), no additional unresolved TA sources were added to the Kattegat and Danish Straits (sub-basins 1-6, Fig. 1). Since these basins have quite short residence times (Gustafsson, 2000), internal TA generation will not significantly influence concentrations from conservative mixing between inflowing saline water from the North Sea and outflowing fresher waters from the Baltic Proper. For that reason, it is not feasible to constrain any unresolved sources in these areas, although the same processes that generate TA in the remaining Baltic Sea should apply to these sub-basins as well.

2.2.3 Merits and limitations of using two models

Using a mass-balance approach, BALTSEM connects external sources, transports between basins, and internal cycling of carbon, nutrients, and TA within each sub-basin. The model is thus highly useful to quantify fluxes – resolved as well as unresolved – on a basin- and system-scale. It is furthermore an invaluable tool when investigating multi-stressor effects on the ecosystem in future scenario calculations. However, the lack of parameterizations for TA production and consumption related to sedimentary Fe-S cycling means for example that there is no S burial – a process that represents a net TA source. The RTM on the other hand resolves these processes in detail and quantifies the fluxes at specific sites. ~~At present, i~~It is not feasible to upscale such site-specific fluxes to the system-scale. Moreover, it would require that the fate of all components contributing to the TA efflux calculated by the RTM should be evaluated in BALTSEM. We know that a substantial part of the TA efflux from the sediment is due to components that are reoxidized in the water column. Only a full coupling between both models, which is currently not feasible as discussed below, would allow monitoring the fate of these components. We therefore use only that part of the TA efflux that is due to a sedimentary source that is permanent on the time scale of interest, i.e. the burial of reduced S. In the present study, 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 TA ~~— in the present study~~ flux~~es~~ due to S burial and computed by the RTM was subsequently upscaled to cover a certain bottom type in the relevant sub-basin (i.e., the total muddy sediment area~~cf. Section 2.1.1~~). This was done by multiplying the net TA ~~efflux~~generation resulting from S burial (mmol m^{-2} y^{-1}) by the muddy sediment area of the Baltic Proper (Table 1).

~~This approach means that it is for the first time possible to estimate~~The RTM calculations ~~allow for~~provide the first ~~time~~ estimates of ~~how~~ the impact of benthic Fe-S processes ~~influence~~ on TA in the Baltic Sea, and in particular clarify to what extent the previously mentioned unresolved sources can be associated with S burial. Other processes that influence TA (e.g. redox reactions involving N) are included in both models. Although benthic N cycling is described in more detail in the RTM, it is in this case preferable to use the fluxes as calculated by BALTSEM. One reason is to take advantage of the coupled physical-biogeochemical approach as described above, so that the source of the NO_3^- ~~nitrate~~ can be identified on a basin scale. On top of that, denitrification rates at F80 are not representative for the entire sub-basin.

Ideally the RTM would be dynamically coupled to BALTSEM, but this is currently not feasible for two reasons: ~~The main reason is that~~First and foremost, direct coupling would require 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 numerous new state variables to BALTSEM (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. ~~First~~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. Second,~~ calibration of the RTM in various parts of the Baltic Sea would be problematic because of an insufficient coverage of sediment data. ~~Thus~~Therefore, the two models are not directly coupled to one another but instead used independently.

3 Results

3.1 Sediment and RTM calculations

Both the model- and observation-based estimates indicate that between 1970 and 2009, on average 291-295 mmol S m^{-2} has annually been buried, leading to a TA generation of 582-590 mmol m^{-2} y^{-1}. This corresponds to a TA flux of ~43.2-43.8 Gmol y^{-1} from muddy sediments (Table 2). The model further suggests that virtually all of the S solids are present in the form of

FeS_2. Of the 291 mmol m^{-2} y^{-1} of S being buried, only 56% was formed in situ, whereas the remaining 44% was deposited as a result of the shuttling of Fe in the form of FeS_2 to the deep basin (Lenz et al., 2015a). However, as BALTSEM does not resolve FeS_2 formation in either the water column or sediment, both need to be included when estimating the unresolved TA source due to SO_4^{2-}~~sulfate~~ reduction and S burial.

In line with other studies (e.g. Jørgensen, 1977), the vast majority of reduced S produced through SO_4^{2-}~~sulfate~~ reduction was reoxidized in either the sediment or the overlying water. On average, only 10.2% was buried, but there was strong temporal variability in this percentage (Table 3). The fraction of S solids being buried was highest under eutrophic but non-euxinic conditions (i.e. period III; 40.7%). Since 1981 (period IV), inputs of Fe oxides have decreased, leading to a higher efflux of $\sum H_2S$ and thus less S burial, despite higher SO_4^{2-}~~sulfate~~ reduction rates (SRR). Our results indicate that even under non-euxinic conditions, pyrite formation was limited by the availability of highly reactive ~~iron~~Fe, as is the case in most marine systems (Berner, 1984; Raiswell and Canfield, 2012) This limitation was confirmed by the difference between potential and simulated S formation rates (Table 3), where the former indicates the amount of solid S that could have formed based on the other modeled sources and sinks of $\sum H_2S$. It is thus indicative of the amount of S mineral formation under unlimited Fe^{2+} supply.

In the period 1970-2009, S burial could on average only explain 328 mmol m^{-2} y^{-1} of TA generation (Table 3; using a 1:2 ratio between S burial and net TA generation). This was 9.2% of the internally generated TA (3948 mmol m^{-2} y^{-1}), but again clear temporal variations were observed (Table 4). Under the baseline conditions (period I), when little S was buried, it only made up 3.7% of the total TA generation. This percentage increased to 12.4% between 1973-1978 (period II), when more Fe was available, and peaked at 34.5% between 1978-1981 (period III), when both $Fe(OH)_3$ and carbon loadings were high. Since 1981 (period IV), the decrease in $Fe(OH)_3$ loading has further limited S burial, leading to a contribution of only 6.7% of the internally generated TA.

Pore-water profiles of DIC and TA (Fig. 3f,g) indicate that the model is well calibrated for the carbonate system. The 2016 DIC data show a better fit with the modeled profile than the previously published DIC data (Reed et al., 2016), while the reverse is true for both TA data sets. The profiles furthermore show that the model overestimates the buildup of $\sum H_2S$ (Fig. 3c). This can be explained by loss of $\sum H_2S$ during sampling, which is a common problem for anoxic sediments, but also by the chosen lower boundary condition of the model. Whereas the model assumes no gradient with the underlying sediment, the data for 2009 (Jilbert and Slomp, 2013; Lenz et al., 2015b) show a declining trend with depth below 32 cm, suggesting a downward diffusive flux of ~144 mmol $\sum H_2S$ m^{-2} y^{-1} in 2009. When fixed at depth as Fe sulfides, this flux would lead to an additional TA generation of ~288 mmol m^{-2} y^{-1} for 2009. However, given the lack of major S accumulation in the sediment below 32 cm (Jilbert and Slomp, 2013), we do not believe this downward flux contributed greatly to net TA generation over the full period of investigation. ~~Rate profiles of the most important processes contributing to TA (Fig. 3) however show that this buildup of $\sum H_2S$ did not substantially affect sedimentary TA generation, as only marginal amounts of $\sum H_2S$ reacted below 10 cm.~~

Rate profiles of the most important processes contributing to TA (Fig. 3i-p). ~~These rate profiles furthermore~~ show that especially between 1978-1981 (period 3), when OM and Fe inputs were high but bottom waters were still oxic, intense cycling of Fe occurred in the sediments, associated with high TA production and consumption. Dissolved Fe produced from reductive dissolution of amorphous Fe ~~iron~~ oxides during OM degradation either diffused upward, where it reoxidized in the oxic sediments (Fig. 3n), or downward to react with $\sum H_2S$ (Fig. 3o). Well-crystalline Fe ~~iron~~ oxides, assumed to be inaccessible for OM degradation, reacted with $\sum H_2S$ over a wide range, thereby producing additional Fe^{2+} (Fig. 3p).

On a system scale, this cycling of Fe does not lead to net TA generation (Hu and Cai, 2011a), but it may impact the efflux of alkalinity from the sediment that is calculated by the RTM. This flux cannot directly be used to assess the long-term net TA generation that we are interested in, as it is the product of a variety of reversible and irreversible TA generating reactions, such as the intense Fe cycling discussed above. Moreover, its constituents (e.g. HS^-) may become reoxidized in the water column. However, the magnitude and temporal variability of the efflux compared to those of S burial and total TA generation may provide information on its driving processes. Note that the difference between total TA generation and efflux (Table 4; Fig. 4) reflects the buildup of TA in the sediment, as well as loss of TA at depth through burial.

A comparison of their temporal variabilities shows that the benthic TA efflux only partly followed the pattern in S burial (Fig. 4; Table 3). Since 1973, when the efflux was 1901 mmol m^{-2} y^{-1}, it decreased to 1561 mmol m^{-2} y^{-1} in 1978, followed by a sharp increase to 3261 mmol m^{-2} y^{-1} in 1982 and a more gradual increase to 4823 mmol m^{-2} y^{-1} in 2009. Generation of TA throughout the entire sediment column contributed to the calculated efflux (Table 4), to a major extent due to high rates of SO_4^{2-} ~~sulfate~~ reduction at depth (Fig. 3k,m). The methane diffusing upward from deeper sediment layers played a key role here, being responsible for on average ~95% of the CH_4-driven SO_4^{2-} ~~sulfate~~ reduction and ~43% of the total SO_4^{2-} ~~sulfate~~ reduction. The temporal change in spatial pattern of the CH_4-driven SO_4^{2-} ~~sulfat~~e reduction (Fig. 3m) ~~suggests that the role of~~ is a direct result of more SO_4^{2-} being consumed by organic matter degradation since the start of bottom-water euxinia (Fig. 3k, Table 4). This is confirmed by the upward-shifting sulfate-methane transition zone (SMTZ) since the onset of bottom-water euxinia (Fig. 3d; see also Reed et al., 2016), which position matches the ~~upward diffusing CH_4 relative to in situ produced CH_4 has become less important over time, as in 2009~~ highest reaction rates of CH_4-driven SO_4^{2-} ~~sulfate~~ reduction (Fig. 3m) ~~were found at ~8 cm depth rather than at the bottom of the modeled sediment column~~. The minor peak in CH_4-driven SO_4^{2-} ~~sulfate~~ reduction around 5 cm depth in 1973 and 1978, and the slightly more pronounced peak at ~3 cm depth in 1981, are in contrast driven by in-situ produced methane due to methanogenesis (Fig. 3l).

Interestingly, the decrease in efflux between 1973-1978 (period II), which resulted from changes in the Fe ~~iron~~ loading, was not mimicked in either the total TA generation or the amount of S burial, but rather reflected the pattern of the change in TA generation through secondary reactions (Fig. 4). The most important secondary reaction contributing negatively to TA between 1973-1978 was the reoxidation of Fe^{2+}, the rate of which more than doubled during this period (Table 4~~; Fig. 3~~) and which, in contrast to the other dominant reactions, was restricted to the upper cm of the sediment column (Fig. 3n). This indicates that it was the driving force of the lower TA efflux during this period. Although reoxidation of Fe^{2+} consumed even more TA in period III (1978-1981), this was more than compensated for by the concurrent enhanced TA generation due to OM degradation, especially coupled to Fe ~~iron~~ oxide reduction, even though that occurred deeper in the sediment (Fig. 3j; Table 4).

In summary, this discrepancy between sedimentary TA generation due to S burial and modelled effluxes of TA highlights that both represent processes acting at various spatial and temporal scales. Long-term TA generation should be interpreted 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. In contrast, calculated efflux of TA, as well as TA generation through various processes at a specific moment in time within different zones in the sediment, is highly variable and is directly impacted by local coupled dynamics of S, Fe and CH_4 (see also Table 4, Figure 3). While the sedimentary processes are highly relevant to understand the major factors driving short-term TA dynamics, ultimately it is the burial of S that represents a TA source relevant on the long term (see also section 2.2.3).

3.2 BALTSEM calculations

The recalibrated unresolved TA sources as well as the resolved pelagic and benthic TA sources minus sinks in the different sub-basins as calculated with BALTSEM are indicated in Table 5. In total, the recalibrated unresolved source amounts to 2~~57.5~~60 ± 0 Gmol y^{-1} (constant over time),~~,~~ while the total resolved pelagic and benthic sources minus sinks amount to a net source of 1~~19.4~~20 ± 47 Gmol y^{-1} over the 1970-2014 period. For comparison, the riverine TA load amounts to 4~~69.5~~70 ± 62 Gmol y^{-1}. In Fig. 5-6, simulated and observed surface and deep water TA normalized to mean salinity at the corresponding station and water depth (TA_N) and salinity are shown. The normalized TA is used in order to avoid uncertainties related to discrepancies between simulated and observed salinity. Full lines in Fig. 5-6 represent the scenario were the unresolved sources were added as land loads, whereas dashed lines represent the case were these sources were instead modeled as sediment effluxes.

The temporal development of resolved and unresolved TA sources minus sinks throughout the model simulation are shown in Fig. 7. In this simulation, the unresolved sources in the different sub-basins were assumed to remain constant throughout the model run (Fig. 7), while the resolved sources and sinks vary depending on primary productivity, oxygen conditions, denitrification rates, and other biogeochemical processes included in the model~~ (Fig. 5-6)~~. Despite the constant unresolved sources, simulated TA_N concentrations generally reproduce observed values. Exceptions are the simulated TA_N concentrations in the Kattegat and the Gotland Sea in the 1980~~'~~s, where actual concentrations are overestimated, and TA_N concentrations in the Bothnian Sea and Bay that are underestimated in the last ten-year period (Fig. 5-6).

There is an overall long-term increase in the resolved net TA generation in sediments and water column combined (Fig. 7), reflecting the ongoing eutrophication and overall deteriorating oxygen conditions of the Baltic Sea. The resolved net pelagic TA source increases in the period 1970-2000 in response to an increased primary production and then levels out and slightly declines in the last decade. The increased resolved benthic source in the last decade on the other hand is a response to deteriorating oxygen conditions resulting in increased TA generation through denitrification and SO_4^{2-}~~sulfate~~ reduction. Sulfate reduction in the BALTSEM model is however not an irreversible source, since sulfidic waters can be reoxidized by deep water inflows, thus consuming TA and reversing the source.

4 Discussion

4.1 Use of BALTSEM and RTM in the context of this work

Given the detailed presentation of sedimentary processes and effluxes in ~~section~~ Section 3.1, one may wonder why only S burial is used in the coupling to BALTSEM. After all, the RTM calculations include many processes other than S burial. However, to study the impact of sedimentary TA generation on the long-term TA development in the Baltic Sea, we need to take into account only those processes that are relevant to accomplish this task.

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 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~~BALTSEM includes many processes, producing and consuming TA both reversibly and irreversibly on short time scales and in many boxes within each sub-basin of the Baltic Sea. The net result of these simulations, i.e. the long-term development of TA in various sub-basins, is what we compare to observations. Similarly, the RTM calculates net TA generation due to various reversible and irreversible processes. 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~~.

This means that in this context we only need to consider the processes from the RTM that are a) irreversible on the time scale of interest (i.e., decades); and b) not included in BALTSEM. Burial of Fe sulfides (Hu and Cai, 2011a) is the only major process that falls in this category. Denitrification using an external NO_3^- source, the other main pathway for net TA generation (Hu and Cai, 2011b) is already included in BALTSEM. Many other sedimentary processes produce or consume TA (~~Eq.~~Table S1-S2~~2~~, supplementary material; Soetaert et al., 2007), but they are not irreversible on the relevant time scale. Their dynamics are, however, highly interesting to discuss as they help determine what limits net sedimentary TA generation, and which processes mainly drive the effluxes of TA and other constituents to the water column. Note that this irreversibility is also a reason why we do not use these effluxes as input to BALTSEM. In addition, they are already partly included in BALTSEM, e.g. in the case of $\sum H_2S$ produced from SO_4^{2-} ~~sulfate~~ reduction.

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 pore water 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 pore water profiles show that site F80 has a relatively high rate of organic matter deposition and alkalinity regeneration when compared to 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 maximum estimate of the contribution of S burial to the overall TA budget of up to 26%.

Although a full coupling between the two models is not a realistic goal at the moment, the development of sediment processes in BALTSEM is decidedly a highly desirable future goal. In particular, the inclusion of sedimentary Fe-S dynamics and related phosphorus (P) cycling would serve to improve our understanding of both TA and P dynamics on a system scale. The present study can be seen as an intermediate step towards a more detailed (if not complete) model 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.

4.2 Sulfur burial and TA generation in the Baltic Proper

While mineralization in the sediments occurs everywhere where there is labile organic matter, permanent burial of organic matter as well as other solids such as Fe sulfides should predominantly occur in muddy sediments. Consequently, the part of the unresolved TA source that is a result of ~~sulfur~~ S burial should be released from muddy sediments rather than from the entire sediment surface area of the Baltic Sea. Our RTM calculations in combination with observations from site F80 in the Baltic Proper (sub-basin 7-9 in Fig. 1) provide the first estimate of TA generation resulting from S burial in Baltic Sea sediments (582-590 mmol m^{-2} y^{-1}). Assuming that the calculated TA generation resulting from S burial is representative only for the muddy sediment area in the Baltic Proper (74300 km^2; Table 1), the total annual flux in this area is ~44 Gmol y^{-1}. The calibrated unresolved TA source in the Baltic Proper amounts to ~~166~~ 170 ± 0 Gmol y^{-1} according to the BALTSEM model (Table 5).

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 lower in the “land loads” case compared to the “sediment release” case.

In the sediment release case, the unresolved TA source in the Baltic Proper (170 ± 0 Gmol y^{-1}) ~~TA source in the Baltic Proper~~ corresponds to a flux of 730 mmol m^{-2} y^{-1} if the source is distributed evenly over the entire sediment surface (228000 km^2). However, if the unresolved source is instead constrained only to muddy sediments, the flux would amount to 2236 mmol m^{-2} y^{-1}, which is far above the long term mean flux due to S burial as obtained by RTM calculations. Even during peak pyrite formation periods, S burial only resulted in a source of 1078 mmol TA m^{-2} y^{-1} (Table 3). Furthermore, in a BALTSEM experiment where the unresolved sources were released only from muddy sediments (but at higher rates corresponding to the smaller surface areas), the deep water TA concentrations in particular in the Baltic Proper were overestimated while the surface water TA concentrations were underestimated (not shown). Based on the RTM calculations, TA generation coupled to ~~sulfur~~ S burial could thus ~~cover~~ account for ~~some~~ 26% of the unresolved source at least in this sub-area of the system. The remaining unresolved TA source of ~74% could possibly be explained by underestimated river loads or submarine groundwater discharge of TA (e.g. Szymczycha et al., 2014). We have no data to quantify these fluxes, however.

In the BALTSEM simulation, the unresolved ~~TA source in the Baltic Proper corresponds to a flux of 730 mmol m^{-2} y^{-1} if the source is distributed evenly over the entire sediment surface (228000 km^{2}). However, if the unresolved source is instead constrained only to muddy sediments, the flux would amount to 2236 mmol m^{-2} y^{-1}, which is far above the long term mean flux due to S burial as obtained by RTM calculations. Even during peak pyrite formation periods, S burial only resulted in a source of 1078 mmol TA m^{-2} y^{-1} (Table 3). Furthermore, in a BALTSEM experiment where the unresolved sources were released only from muddy sediments (but at higher rates corresponding to the smaller surface areas), the deep water TA concentrations in particular in the Baltic Proper were overestimated while the surface water TA concentrations were underestimated (not shown).~~

4.3 Reversible versus irreversible sedimentary processes generating TA

As demonstrated by both simulated and observed sediment profiles at F80, a transition from hypoxic to euxinic conditions around 1980 resulted in a strong increase in both solid phase S and Fe burial (Reed et al., 2016). Furthermore, the molar S to Fe ratio of ~2 suggests formation and burial of mostly FeS$_2$. Both FeS$_2$ and FeS can be formed from reactive Fe^{2+} and sulfide produced during Fe(OH)$_3$ and SO$_4^{2-}$~~sulfate~~ reduction, respectively. These redox reactions ultimately result in net TA generation (~~Eq. S1-S22~~Table S1-S2, supplementary material). Another possible pathway is that methane (formed by methanogenesis) is oxidized anaerobically by reduction of either SO$_4^{2-}$~~sulfate~~ or Fe(OH)$_3$ (Slomp et al., 2013; Egger et al., 2015b), and Fe and sulfide can then be sequestered in the form of e.g. FeS$_2$. Results from the RTM indicate that CH$_4$ and organic matter are both important electron donors at F80 CH$_4$ oxidation contributes to on average 43.8% of total SRR, and occurs at greater depth than SO$_4^{2-}$~~sulfate~~ reduction through organic matter degradation (Fig. 3k,m). Iron-mediated anaerobic oxidation of methane is not included in the set of reactions of this RTM. Previous work has indicated that this process mainly occurs in organic-poor sediments depleted in SO$_4^{2-}$ (Riedinger et al., 2014; Egger et al., 2017). These conditions are not met at F80, rendering an important role for this process unlikely.

Apart from such eutrophication-induced changes in the coupled Fe-S cycling, increasingly euxinic conditions also influence manganese (Mn) sequestration in sediments. Dissolved Mn^{2+} can be sequestered in the form of Mn carbonates (MnCO$_3$). If this occurs, the TA generation associated with the reduction of manganese dioxide (MnO$_2$; 2 moles of TA per mole of MnO$_2$; Table S1-S2~~Eq. S1-S22~~, supplementary material) is completely compensated by the TA sink associated with carbonate removal. However, under euxinic conditions, manganese sulfide (MnS) can be formed if the sulfide availability exceeds the Fe^{2+} availability (Lenz et al., 2015b). Indeed, long-term sediment records indicate a relation between euxinic periods in Baltic Sea deep waters and burial of Mn sulfides in the forms of both rambergite and alabandite (Lepland and Stevens, 1998). As opposed to burial of $MnCO_3$, burial of MnS results in a net TA generation comparable to that of FeS_2 burial. In the RTM, we did not investigate the possible impact of MnS formation on TA generation as the sediment record at F80 does not show substantial Mn enrichments in the surface, despite higher sulfide than Fe^{2+} availability (Lenz et al., 2015b).

Ammonium, ΣH_2S~~sulfide~~, Fe^{2+} and Mn^{2+} are rapidly oxidized if oxygen is supplied to anoxic waters. The result is a TA sink that compensates the TA generation by anaerobic mineralization. Precipitates such as FeS and FeS_2 can also be oxidized but this is generally a slower process, especially in the case of FeS_2 (Millero et al., 1987; Wang and Van Cappellen, 1996). Moreover, these S minerals are embedded in organic-rich, ΣH_2S producing sediments. This reduces the impact of possible reoxygenation of the sediment for extended periods of time, implying that the TA source that results from S burial is stable. Sediment cores indicate the presence of Fe sulfides – in particular FeS_2 – in the top three meters of Gotland Sea deep water sediments (Boesen and Postma, 1988) as well as in the top 10 m of deep Bornholm Basin sediments and the top 27 m of Landsort Deep sediments (Egger et al., 2017), all corresponding to roughly 8000 years. In our model results, FeS_2 is the dominant form of S in the sediment. Our work also shows that re-oxidation of reduced S never exceeds 0.5% between 1970-2009, irrespective of whether S solids or the total reduced S pool (i.e., including $\sum H_2S$) is investigated (Table ~~S2~~S5, supplementary material).

Vivianite formation is another process that generates TA in a net sense. The presence of vivianite in sediment cores (Egger et al., 2015a) indicates that this mineral can be stable upon burial. However, vivianite dissolves in the presence of ΣH_2S~~sulfide~~ (Dijkstra et al., 2018), excluding its burial to be a long-term TA source at F80. It could however be a stable TA source at locations where ΣH_2S rather than Fe availability limits pyrite formation, such as the Bothnian Sea (Egger et al., 2015a).

Calcifying organisms that build calcium carbonate ($CaCO_3$) shells have a large influence on the carbonate system in many marine areas, as illustrated e.g. by high TA fluxes related to $CaCO_3$ formation and dissolution in the North Sea (Brenner et al., 2016). $CaCO_3$ formation results in a TA drawdown in the productive layer, and a TA source where the shells are dissolved. Burial of $CaCO_3$ shells is a net TA sink on a system scale. In the Baltic Sea, however, ~~calcifying plankton~~planktonic calcifiers ~~species~~ are largely absent – likely because of low saturation values of calcite and aragonite in winter (Tyrrell et al., 2008). In the RTM, $CaCO_3$ dissolution and precipitation is included, based on observed sedimentary $CaCO_3$ contents of ~200 μmol g^{-1} (Fig. 3e; see Reed et al., 2016 for further details). The prescribed input of 86 mmol m^{-2} y^{-1} in combination with prevailing conditions in the sediment led to a net TA loss due to $CaCO_3$ dissolution, which is on average only -0.01 mmol m^{-2} y^{-1} (data not shown). For this reason, we have not included the effects of $CaCO_3$ precipitation and dissolution in our analysis.

4.4 Long-term development of TA in the Baltic Sea

Several studies indicate essentially linear TA-salinity relations in Baltic Sea surface water (Ohlson and Anderson, 1990; Thomas and Schneider, 1999; Perttilä et al., 2006; Beldowski et al., 2010). Long-term TA increases that are not connected to salinity are however apparent from observed TA-salinity relations (Fig. 8; Table ~~S4~~S7-~~S5~~S8, supplementary material). Furthermore, Müller et al. (2016) ~~computed a 3.4 µmol kg^{-1} y^{-1} surface water~~found generally increasing TA concentrations decoupled from salinity in the Baltic Sea ~~increase in the Baltic Proper and a 7 µmol kg^{-1} y^{-1} increase in the Gulf of Bothnia~~ over the past two decades.

The resolved pelagic and benthic TA sources minus sinks in the BALTSEM calculations (Fig. 7) on average increase by approximately 3 Gmol y^{-1} in the 1970-2014 period. Furthermore, the RTM calculations (Table 3) indicate that ~~sulfur~~ S burial can increase by a factor of four after a transition from oxic to anoxic/euxinic conditions, and even by an order of magnitude during this transition if both Fe ~~iron~~ oxide and organic matter loadings are enhanced. Thus, the fraction of the unresolved source that is a result of ~~sulfur~~ S burial should be quite variable depending on mineralization rates and oxygen conditions in different areas of the Baltic Sea as well as during different periods in time.

Anaerobic mineralization occurs in sediments even if the overlying water is oxic, and for that reason TA release coupled to ~~sulfur~~ S burial does not exclusively occur from sediments covered by sulfidic waters. In fact, our results indicate highest S formation rates under eutrophic, but non-euxinic conditions (Table 3). However, large-scale and long-term changes in TA generation related to changes in ~~sulfur~~ S burial are mainly expected to occur in areas experiencing transitions between oxic and anoxic conditions and in addition as a result of changes in Fe ~~iron~~ loadings (Lenz et al, 2015a). Hypoxic and anoxic conditions in the Baltic Sea water column – as well as rapid transitions between oxic and anoxic conditions – occur primarily in the deep basins of the Baltic Proper, although episodes of oxygen depletion can also occur in the deep water of in particular the Gulf of Finland, as well as in many eutrophic coastal fjords and bays.

The long-term TA decrease in the Gotland Sea in the 1980~~'~~s coincided with a decreasing salinity (Fig. 5 and S1) as well as improved oxygen conditions in large volumes of the deep water (not shown). During this period, stratification was considerably weakened and as a result the halocline depth in the Baltic Proper increased, and inflowing new deep water ventilated primarily the upper deep water. Thus, a much larger water volume than usual was well ventilated (e.g. Stigebrandt and Gustafsson, 2007). It is possible that during this period, ~~sulfur~~ S burial and associated TA generation was considerably weakened. A very strong TA increase observed in the early 1990~~'~~s coincides (more or less) with a strengthened stratification due to salt water inflows in 1993. A rapid deterioration of oxygen conditions followed because of a suppressed deep water ventilation during periods of strong stratification. This development towards increasingly anoxic/euxinic conditions could potentially cause a large response in terms of TA generation.

It is however likely that the observed TA decline in the 1980~~'~~s followed by the strong TA increase in the 1990~~'~~s is exaggerated because of unreliable measurements before 1993. After that, the precision of TA measurements appears to have increased considerably as is evident from the relatively low scatter in TA values after 1993 as compared to before 1993 (cf.

Müller et al. (2016), their Fig. 3). In particular, we find in Fig. 6 that even in the Kattegat deep water the observed TA concentrations in the period ~1985-1992 are comparatively low. While the Kattegat surface waters are heavily influenced by outflowing Baltic Proper water, the Kattegat deep water is affected only very marginally. Furthermore, the observed TA values from the Gotland Sea deep water in approximately the same period are considerably lower than our modeled values (Fig. 6).

TA is also influenced by atmospheric deposition~~s~~ on the water surface due to emissions from land and ships (Hassellöv et al., 2013; Hagens et al., 2014). Deposition of S and N oxides represents a TA sink, while ΣNH_4^+ deposition is a TA source. The net effect is a TA sink; the impact peaked in the 1980~~'~~s, but has since then diminished due to reduced land emissions (Omstedt et al., 2015). According to our BALTSEM calculations, the TA sink related to acidic depositions has declined from approximately -40 Gmol y^{-1} in the 1980~~'~~s to -10 Gmol y^{-1} in the past decade. This reduced TA sink thus contributes to the increasing TA concentrations in the Baltic Sea.

Riverine TA concentrations can increase as a result of enhanced weathering of carbonate and silicate rocks in the catchments. The rate of weathering depends on temperature, precipitation, soil organic matter contents, and deposition of acids (Ohlson and Anderson, 1990; Dyrssen, 1993; Sun et al., 2017). Average TA loads from Swedish rivers in 1985-2012 and Finnish rivers in 2001-2012 amount to 42 and 15 Gmol y^{-1} respectively (Fig. S2, supplementary material), together corresponding to some 12% of the total TA load (~470 Gmol y^{-1}) to the system. There was a strong long-term increase in the flow-normalized TA loads from Swedish rivers – approximately 21% over the period 1985-2012. In Finnish rivers on the other hand, there was no increase in the period 2001-2012. Because of a generally poor availability of river data from other countries around the Baltic Sea, we have no clear understanding of the long-term TA development in e.g. the great rivers in the south-eastern Baltic Sea (where also the highest TA concentrations are generally observed).

Riverine TA concentrations in the BALTSEM model were calculated from observed monthly mean values only in the period 1996-2000. If the long-term increasing trend observed for TA loads in Swedish rivers is also representative for rivers in e.g. the south-eastern Baltic Sea, this would signify that the model is forced by too low riverine TA concentrations in the last decade but on the other hand too high concentrations in the first couple of decades. It is plausible that changes in river water properties are responsible for at least part of the overall increasing TA concentrations in the Baltic Sea. This could in particular be the case for the Bothnian Sea and Bay where simulated TA in the last decade is underestimated by the BALTSEM model (Fig. 5-6).

4.5 ~~Implications~~Simulations of future scenarios

High productivity and deep water oxygen consumption rates favor TA generating anaerobic mineralization processes. One potential consequence is that a large-scale recovery from eutrophication could reduce the CO_2 buffering capacity of a marine system and thus also reduce the atmospheric CO_2 sink and surface water pH.

In this section we investigate how the simulated TA in BALTSEM responds to two different nutrient load scenarios: 1. The Business As Usual (BAU) scenario with high nutrient loads throughout the 21st century, and 2. The Baltic Sea Action Plan (BSAP) scenario with large reductions in ~~nitrogen~~ N and ~~phosphorus~~ P loads (Fig. S3, supplementary material). We use the

ECHAM5 A1B #1 scenario for CO_2 emissions and climate change downscaled for the Baltic Sea region (cf. Omstedt et al., 2012). The A1B emission scenario represents a socio-economic development producing medium CO_2 emissions where the atmospheric CO_2 partial pressure (pCO_2) reaches some 700 µatm by the year 2100 (Fig. S4, supplementary material). The unresolved TA source is kept constant throughout these simulations. This means that any simulated changes in TA are related to changes in river loads and exchange with the North Sea, as well as changes in TA producing/consuming biogeochemical processes that are included in BALTSEM (production, mineralization, denitrification, nitrification, SO_4^{2-}~~sulfate~~ reduction, ΣH_2S~~sulfide~~ oxidation, etc.).

According to the BALTSEM simulations, the surface and deep water temperatures in the Gotland Sea will increase by approximately 3 degrees over the 21st century, while salinity is reduced by more than 2 (Fig. S5, supplementary material). Surface water phosphate concentrations will decline by ~0.2 µmol kg^{-1} in the BSAP scenario, resulting in a reduced primary production and increased deep water oxygen concentrations (Fig. S6, supplementary material). The reduced productivity and large-scale recovery from anoxic deep water conditions in the BSAP scenario will also ~~will~~ have large consequences for TA and in extension CO_2 buffer capacity and pH. Towards the final decades of the simulations, surface water TA in the BAU scenario exceeds that in the BSAP scenario by ~150 µmol kg^{-1} (Fig. 9). As a result, the surface water pH is reduced by 0.1 units more in the BSAP than in the BAU scenario.

These scenario simulations do not include changes in TA generation resulting from changes in S burial driven by productivity and Fe-oxide availability, since these processes are not resolved in BALTSEM. To investigate how the sediment, and more specifically S formation and burial, will respond to changes in Fe ~~iron~~ and organic carbon loadings, we ran the RTM for an additional 40 years under the present environmental conditions, as well as under a range of changes in these loadings. This sensitivity analysis (Table 6) shows that reverting the productivity regime to pre-1978 conditions decreases the calculated TA efflux by ~50%, a direct result of less organic matter degradation, whereas S burial is hardly impacted as it is still limited by Fe availability. 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 again the decoupling between short-term flux dynamics and long-term TA generation, as discussed extensively in Sections 2.2.3 and 3.1. ~~-~~Increasing the Fe-oxide loading to the peak values of 1981 slightly lowers the TA efflux while more than doubling S burial, a direct results of a higher Fe availability. In summary, our sensitivity analysis confirms ~~-~~that the form and ~~amount~~ rate of Fe ~~iron~~ ~~dynamics~~ input exerts the dominant control on S burial and long-term TA impacts, whereas the ~~amount~~rate of organic matter input mainly drives ~~is the major driver of~~ the short-term variability in TA effluxes. It also ~~stresses~~ highlights that sedimentary TA generation due to S burial and modelled effluxes of TA should be regarded as occurring on various temporal scales.

It is a simple exercise to examine the sensitivity of pH to further changes in TA. Using the CO2SYS software (~~Lewis and Wallace, 1998~~van Heuven et al., 2011; ~~http://cdiac.esd.ornl.gov/oceans/co2rprtnbk~~ http://cdiac.ess-dive.lbl.gov/ftp/co2sys/CO2SYS_calc_MATLAB_v1.1/), and assuming that the surface water pCO_2 is in equilibrium with the atmosphere, a surface water pCO_2 of 700 µatm and TA of 1425 µmol kg^{-1} (as at the end of the BSAP scenario) results in a surface water pH of 7.~~77~~80, ~~-~~assuming a salinity of 5.2 and temperature of 11 °C (cf. Fig. S5)~~which is very close to the~~

~~simulated annual mean pH (Fig. 9)~~. For example, decreasing the surface water TA to 1325 or 1225 µmol kg^{-1} results in pH values of 7.~~74~~ 77 or 7.~~70~~ 73 respectively. On the contrary, in order to completely compensate for the CO_2-induced pH decline resulting from an atmospheric pCO_2 increase to ~700 µatm in the A1B scenario, the surface water TA would have to increase to ~~almost 3000~~approximately 2800 µmol kg^{-1} – which is a completely unrealistic TA concentration for surface water in the Gotland Sea regardless of productivity and oxygen conditions. It is for that reason beyond any doubt that the only possible way to avoid acidification of open Baltic Sea waters is to implement large reductions in CO_2 emissions. Although there is a larger pH decline in the BSAP than in the BAU scenario, the possible negative influence must be considered to be of a marginal importance compared to the vast benefits for Baltic Sea ecosystems following reduced deep water dead zones.

5 Summary and concluding remarks

Model calculations have been used to constrain the sedimentary TA efflux in the Baltic Proper, and to examine how this efflux has developed over a 40-year period in relation to eutrophication and oxygen deterioration. In particular, the net TA source related to permanent ~~sulfur~~ S burial in the sediment was calculated using a reactive transport model. Furthermore, the physical-biogeochemical BALTSEM model was used to estimate future TA concentrations and pH levels depending on the development of nutrient loads to the system.

The sedimentary TA generation undergoes large changes depending both on organic matter loads and oxygen conditions. Especially large changes occur during transitions between suboxic and euxinic conditions. Some of these changes are reversible, while others – such as a permanent ~~sulfur~~ S burial – result in a net TA generation. Our calculations imply that ~~sulfur~~ S burial in the Baltic Proper has resulted in an average net TA generation of ~~approximately~~ up to 44 Gmol yr^{-1} in the period 1970-2009. This flux covers ~26% of the missing TA source in this basin (as estimated by the BALTSEM model).

When comparing the BAU and BSAP nutrient loads in combination with the A1B scenario for CO_2 emissions, we find a larger pH reduction in the BSAP case than in the BAU case (by approximately 0.1 pH unit). This is a response to reduced signs of eutrophication and particularly substantial improvements in deep water oxygen conditions: In our calculations the gradual decline in anaerobic mineralization following improved oxygen condition results in a reduced TA generation and thus a reduced buffer capacity for atmospheric CO_2 in the Baltic Sea. Sedimentary S burial is not resolved in the BALTSEM model. Additional scenario calculations were for that reason performed with the RTM; the results indicate that S burial and long-term effects on the sedimentary TA efflux are primarily controlled by the Fe ~~iron~~ cycle, while short-term changes in the TA exchange between sediments and the water column mainly depend on organic matter inputs.

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Tables

Table 1. Total sediment areas and muddy sediment areas (1000 km^2). The muddy sediment areas are based on Al-Hamdani and Reker (2007). Sub-basins according to Fig. 1.

Sub-basins	1-3 (KT)~~1-3~~	4-6 (DS)~~4-6~~	7-9 (BP)~~7-9~~	10 (BS)~~10~~	11 (BB)~~11~~	12 (GR)~~12~~	13 (GF)~~13~~	1-13 (EBS)~~1-13~~
Sediment area	22.2	19.3	227.6	67.0	36.6	17.5	23.7	413.9
Muddy ~~sediment~~ area	8.5	2.3	74.3	8.8	13.3	8.7	8.8	124.5

Table 2. Estimated S burial (mmol m^{-2} y^{-1}) and associated TA generation (Gmol y^{-1}) for site F80 (58.0000˚N, 19.8968˚E) between 1970 and 2009. Both S contents and dating were taken from Lenz et al. (2015b). The basin scale calculation was based on the total muddy sediment area for the Baltic Proper in BALTSEM of 74300 km^2 (Table 1). Numbers between brackets represent S burial due to in situ S formation only, thus excluding S burial due to FeS_2 deposition.

Source	Sulfur burial (mmol m^{-2} y^{-1})	Total alkalinity generation (Gmol y^{-1})
observations	295	43.8
model	291 (164)	43.2 (24.4)

Table 3. Estimated depth-integrated SO_4^{2-}~~sulfate~~ reduction (SRR), ~~sulfur~~ S re-oxidation (S-OX) and S^0 disproportionation rates (S^0-dispr), as well as $\sum H_2S$ efflux (all in mmol S m^{-2} y^{-1}), as derived from the one-dimensional reactive transport model (Reed et al., 2016) for the periods 1970-1973 (baseline; I), 1973-1978 (start change in Fe loading; II), 1978-1981 (eutrophication but pre-euxinia; III) and 1981-2009 (eutrophication and euxinia; IV). The difference between SRR (production of reduced S) and the sum of S-OX, S^0-dispr and $\sum H_2S$ efflux (removal of reduced S) is assumed to be representative for the maximum potential S formation. The simulated S formation is derived from the mass balance of the RTM (see Table ~~S3~~ S6 for details).

Period	SRR (mmol m^{-2} y^{-1})	S-OX (mmol m^{-2} y^{-1})	S^0-dispr (mmol m^{-2} y^{-1})	$\sum H_2S$ efflux (mmol m^{-2} y^{-1})	Potential S formation (mmol m^{-2} y^{-1})	Simulated S formation (mmol m^{-2} y^{-1})
I: 1970-1973	1002	1.69	1.87	932	66	37
II: 1973-1978	994	1.63	1.82	845	145	125
III: 1978-1981	1304	0.68	0.77	742	561	539
IV: 1981-2009	2118	0.00	1.63	1942	174	148
Average	1805	0.42	1.61	1614	189	164

Table 4: Estimated TA generation from the reactive transport model integrated over the whole sediment column for the periods 1970-1973 (baseline), 1973-1978 (start change in Fe loading), 1978-1981 (eutrophication but pre-euxinia) and 1981-2009 (eutrophication and euxinia) for the dominant processes, as well as TA generation and efflux (all in mmol m^{-2} y^{-1}).

Primary reactions (all in mmol m^{-2} y^{-1})

Period	OM + NO_3^-	OM + MnO_2	OM + $Fe(OH)_3$	OM + SO_4^{2-}	OM + CH_4
1970-1973	36	21	130	966	24
1973-1978	33	20	361	946	24
1978-1981	23	9	1764	1547	36
1981-2009	0	1	51	2706	103
Average	9	5.67	226	2225	80

Secondary reactions (all in mmol m^{-2} y^{-1})

Period	SO_4^{2-} + CH_4	O_2 + Fe^{2+}	Fe^{2+} + $\sum H_2S$	$Fe(OH)_3$ + $\sum H_2S$	O_2 + $\sum NH_4^+$
1970-1973	1125	-115	-37	35	-145
1973-1978	1125	-307	-131	110	-135
1978-1981	1199	-1175	-567	330	-69
1981-2009	1770	0	-146	184	0
Average	1582	-138	-165	170	-36

Total (all in mmol m^{-2} y^{-1})

Period	Total OM degradation	Total secondary reactions	Total TA generation	Modeled TA efflux
1970-1973	1178	836	2015	1901
1973-1978	1385	636	2022	1683
1978-1981	3381	-300	3081	2361
1981-2009	2861	1800	4661	4423
Average	2547	1401	3948	3674

Table 5. Average ~~R~~resolved and unresolved TA sources minus sinks (SMS) and river loads with standard deviations (Gmol y^{-1}) in 1970-2014 according to the BALTSEM calculations in this study. Sub-basins according to Fig. 1.

Sub-basins	1-3 (KT)	4-6 (DS)	7-9 (BP)	10 (BS)	11 (BB)	12 (GR)	13 (GF)	1-13 (EBS)
Resolved pelagic SMS	8.2 ± 1.5	10~~.2~~ ± 2.0	60~~.4~~ ± 28	8.9 ± 2.9	-0.4 ± 0.4	8.8 ± 3.3	9.8 ± 5.2	1~~05.9~~10 ± 35
Resolved benthic SMS	-2.7 ± 0.2	-2.6 ± 0.4	29~~.3~~ ± 38	-4.7 ± 1.0	-1.0 ± 0.1	-3.1 ± 0.5	-1.7 ± 0.5	13~~.5~~ ± 41
Total resolved SMS	5.5 ± 1.4	7.5 ± 2.0	~~89.7~~90 ± 40	4.2 ± 2.2	-1.4 ± 0.3	5.7 ± 3.0	8.2 ± 3.0	1~~19.4~~20 ± 47
Unresolved SMS	-	-	1~~66.2~~70 ± 0	24~~.5~~ ± 0	6.7 ± 0	2~~5.~~6 ± 0	3~~4.6~~5 ± 0	2~~57.5~~60 ± 0
Total SMS	5.5 ± 1.4	7.5 ± 2.0	2~~55.9~~60 ± 40	2~~8.7~~9 ± 2.2	5.3 ± 0.3	31~~.3~~ ± 3.0	4~~2.8~~3 ± 3.0	3~~77.0~~80 ± 47
River load	21~~.0~~ ± 4.1	13~~.5~~ ± 3.5	220~~16.8~~ ± 38	2~~5.6~~6 ± 3.9	1~~6.7~~7 ± 2.7	9~~5.8~~6 ± 21	80~~.1~~ ± 11	4~~69.5~~70 ± 62

Table 6. Input of Fe-oxides and simulated S burial and TA efflux averaged for the period 2011-2050 under a range of environmental conditions as calculated with the reactive transport model. All values are in mmol m^{-2} y^{-1}.

Scenario	Input of Fe-oxides (mmol m^{-2} y^{-1})	Sulfur burial (mmol m^{-2} y^{-1})	TA efflux (mmol m^{-2} y^{-1})
business-as-usual	60	235	4910
no eutrophication	60	232	2558
pre-1973 Fe loading	20	23	4919
peak Fe loading (1981)	360	534	4816

Figures

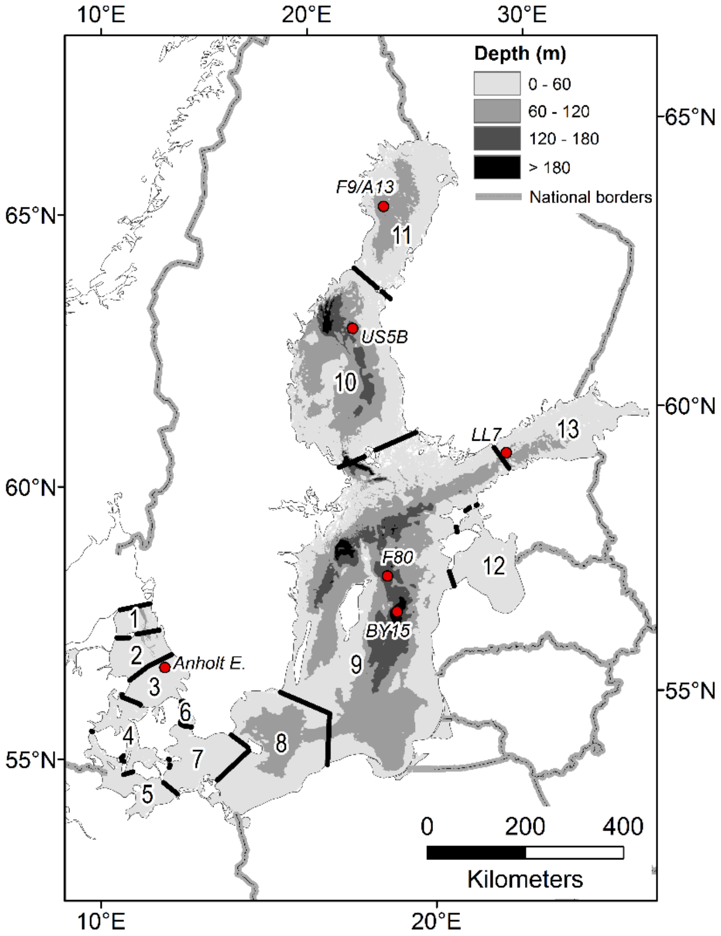

Figure 1: . The Baltic Sea area with sub-basins and monitoring stations. The sub-basins are: 1. Northern Kattegat (NK), 2. Central Kattegat (CK), 3. Southern Kattegat (SK), 4. Samsø Belt (SB), 5. Fehmarn Belt (FB), 6. Öresund (OS), 7. Arkona Basin (AR), 8. Bornholm Basin (BN), 9. Gotland Sea (GS), 10. Bothnian Sea (BS), 11. Bothnian Bay (BB), 12. Gulf of Riga (GR), 13. Gulf of Finland (GF). Some BALTSEM sub-basins are aggregated into larger units in the budget calculations: The Kattegat (KT) includes sub-basin 1–3, the Danish Straits (DS) includes sub-basin 4–6, the Baltic Proper (BP) includes sub-basin 7–9, and the Entire Baltic Sea (EBS) includes all sub-basins.

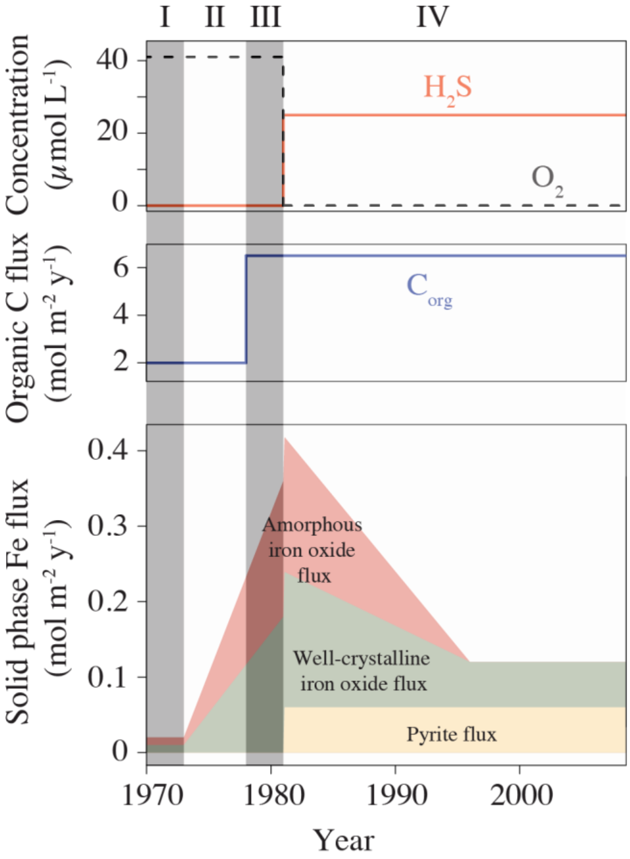

Figure 2: Variability in bottom-water redox conditions, organic carbon and ~~iron~~ Fe inputs between 1970-2009, used to force the reactive transport model at site F80. Numbers indicate the four different time intervals recognized in this study: I. baseline (1970-1973); II. start of change in Fe loading (1973-1978); III. eutrophication but pre-euxinia (1978-1981); IV. eutrophication and euxinia (1981-2009). Figure modified from Reed et al. (2016).

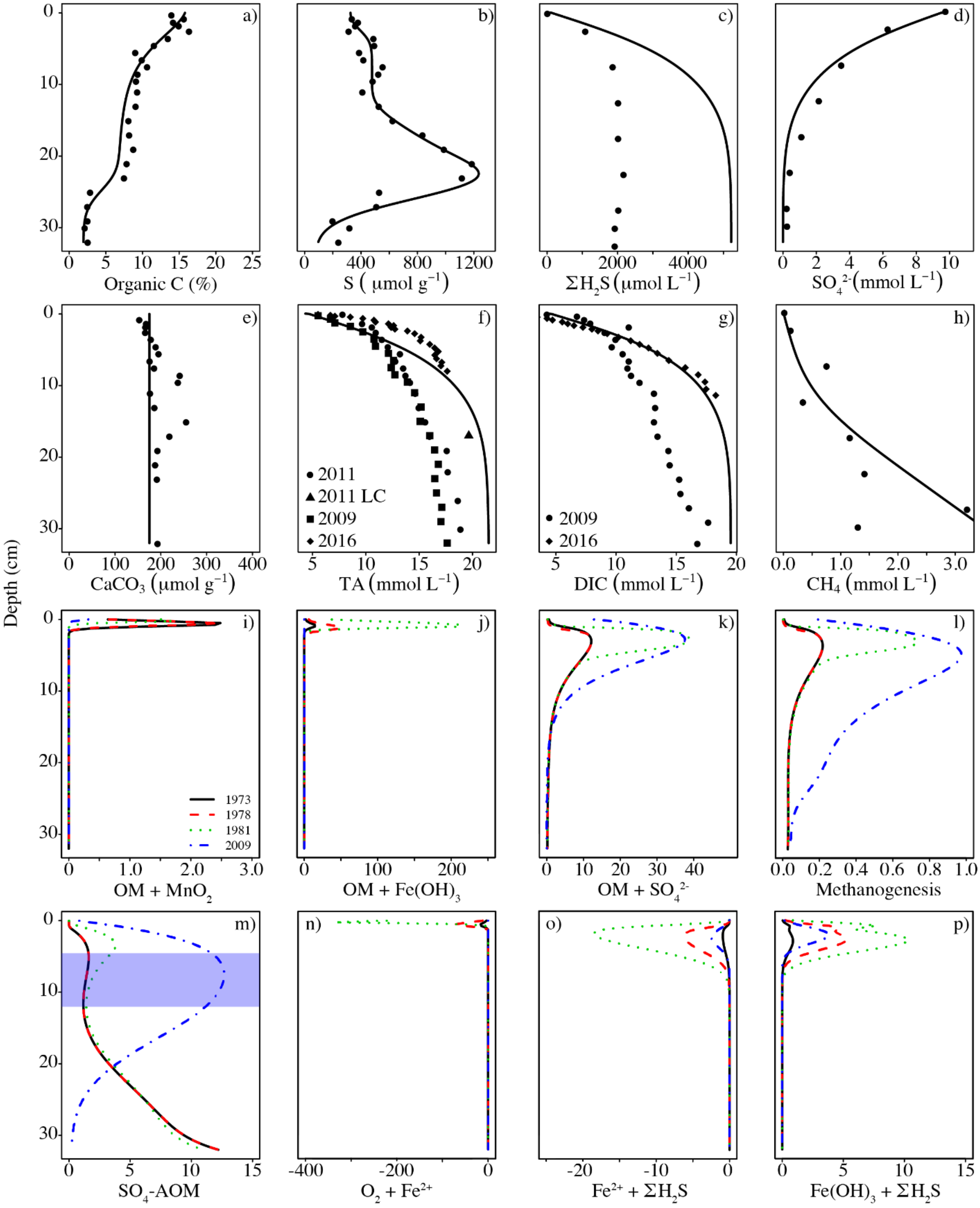
a)
b)
c)
d)
e)
f)
g)
h)
i)
j)
k)
l)
m)
n)
o)
p)
Depth (cm)
0
10
20
30
0 5 10 15 20 25
Organic C (%)
0 400 800 1200
S (μmol g^{-1})
0 2000 4000
ΣH$_2$S (μmol L^{-1})
0 2 4 6 8 10
SO$_4^{2-}$ (mmol L^{-1})
0 100 200 300 400
CaCO$_3$ (μmol g^{-1})
● 2011
▲ 2011 LC
■ 2009
◆ 2016
5 10 15 20
TA (mmol L^{-1})
● 2009
◆ 2016
5 10 15 20
DIC (mmol L^{-1})
0.0 1.0 2.0 3.0
CH$_4$ (mmol L^{-1})
1973
1978
1981
2009
0 1.0 2.0 3.0
OM + MnO$_2$
0 100 200
OM + Fe(OH)$_3$
0 10 20 30 40
OM + SO$_4^{2-}$
0.0 0.2 0.4 0.6 0.8 1.0
Methanogenesis
0 5 10 15
SO$_4$-AOM
-400 -200 0
O$_2$ + Fe^{2+}
-20 -10 0
Fe^{2+} + ΣH$_2$S
0 5 10 15
Fe(OH)$_3$ + ΣH$_2$S

Figure 3: Pore water profiles of selected simulated (solid lines) and observed (dots) variables at site F80 (a-h)~~, as well as ~~; simulated rates of some major processes impacting TA dynamics at the end of the four major time intervals (i-p; all rates in mmol TA dm^{-3} y^{-1}). The blue area in Fig. 3m indicates the sulfate-methane transition zone (SMTZ) in 2009; in the other years, the SMTZ was located around the depth of the below the modeled interval (32 cm). Additional pore water and solid phase profiles were published in Reed et al. (2016). Previously unpublished measurements can be found in Table ~~S2~~ S5 (supplementary material). Dates in a-h indicate sampling dates; LC = long core.

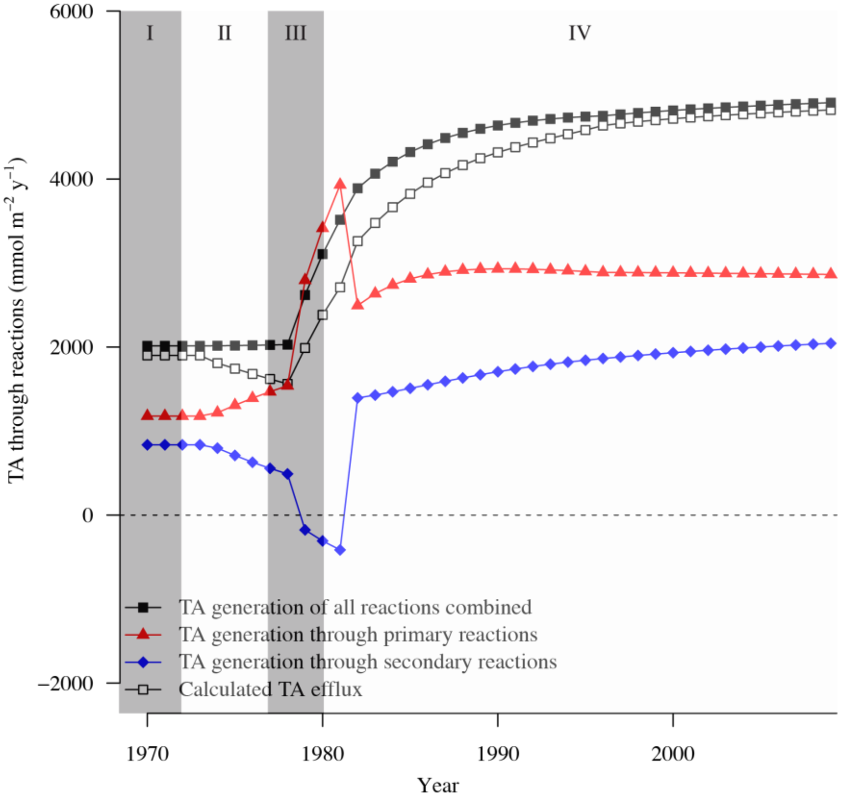

Figure 4: Calculated TA efflux and generation at site F80 integrated over the whole sediment column (all in mmol m^{-2} d^{-1}) due to various biogeochemical processes implemented in the RTM.

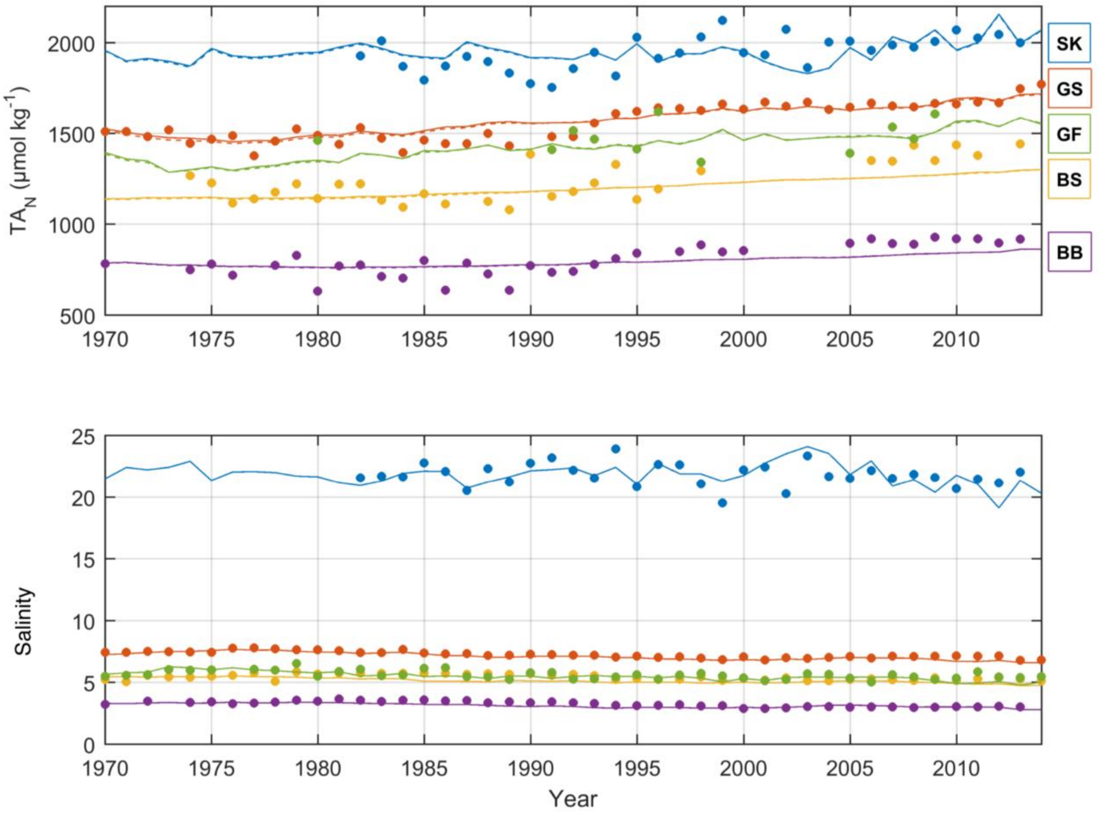

Figure 5: Annual mean observed (dots) and modeled (lines) normalized surface water TA (TA$_N$, µmol kg^{-1}) and salinity in five sub-basins. Full and dashed lines represent the scenarios were the unresolved TA sources are added as land loads or sediment release respectively. Model data from sub-basin 3 (SK), 9 (GS), 10 (BS), 11 (BB), and 13 (GF) are compared to observed data at the Anholt East, BY15, US5B, F9/A13, and LL7 stations respectively.

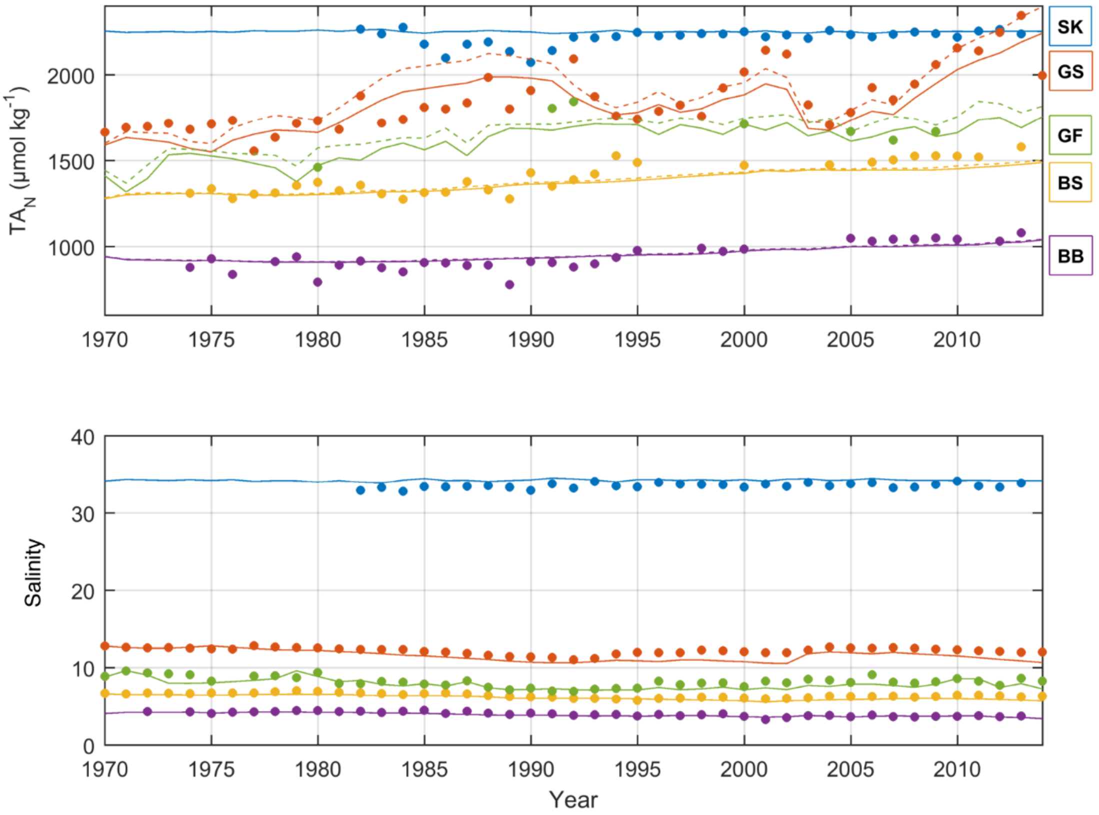

Figure 6: Annual mean observed (dots) and modeled (lines) normalized deep water TA (TA_N, µmol kg^{-1}) and salinity in five sub-basins. Full and dashed lines represent the scenarios were the unresolved TA sources are added as land loads or sediment release respectively. Model data from sub-basin 3 (SK), 9 (GS), 10 (BS), 11 (BB), and 13 (GF) are compared to observed data at the Anholt East, BY15, US5B, F9/A13, and LL7 stations respectively.

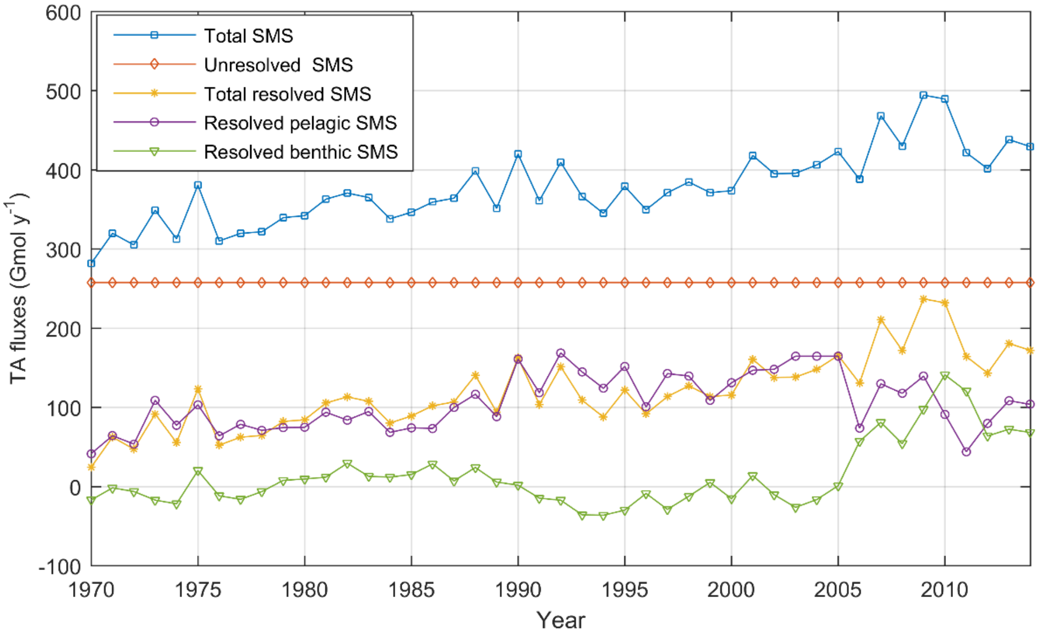

Figure 7: Annual mean TA sources minus sinks (SMS) (Gmol y^{-1}) in the entire Baltic Sea according to BALTSEM calculations: Resolved benthic sources minus sinks (SMS) (green line), resolved pelagic SMS (purple line), total resolved SMS (yellow line), unresolved SMS (red line), and total SMS (blue line).

5

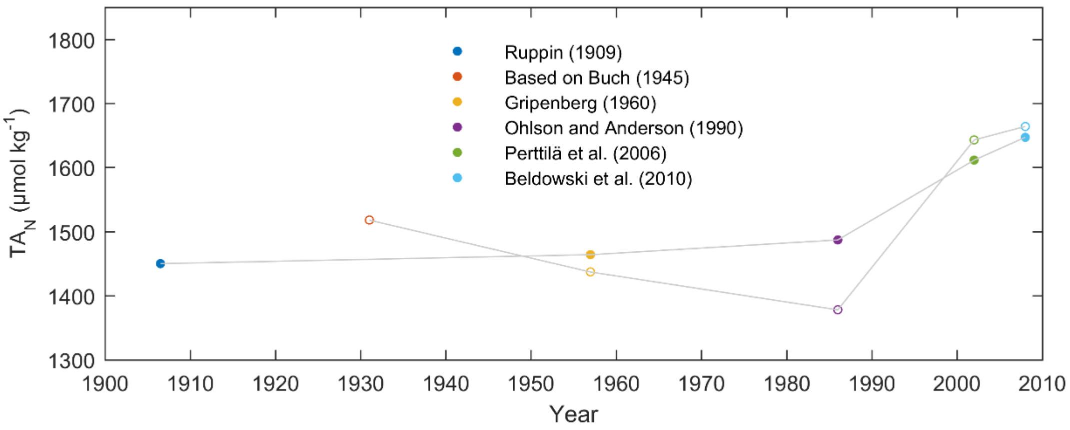

Figure 8: TA concentrations normalized to salinity = 7 (TA$_N$), using the TA-salinity relations for the Baltic Proper – Kattegat (full circles), and Baltic Proper – Gulf of Bothnia (open circles) (cf. Table ~~S4~~S7-~~S5~~S8, supplementary material). The Ruppin (1909) value was based on measurements in 1906-1907 (see Dyrssen, ~~(~~1993~~) for reference~~), while the Buch (1945) value was based on measurements in 1927-1935 (cf. Buch, 1945). The Buch (1945) and Perttilä (2006) values were converted to µmol kg^{-1} from µmol l^{-1}.

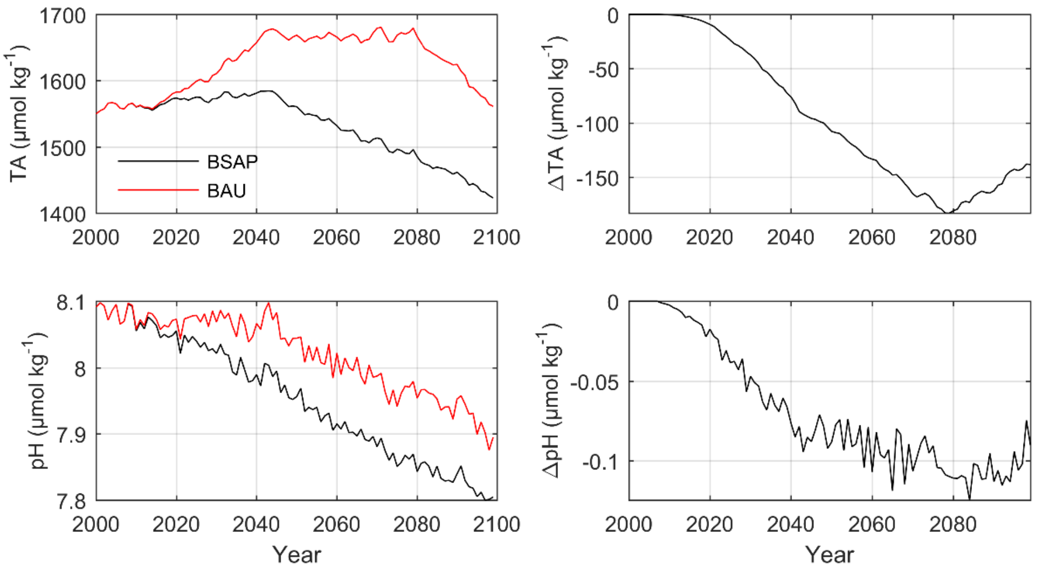

Figure 9: Left: simulated annual mean surface water TA and pH in ~~the Gotland Sea~~ sub-basin 9 (GS) according to the BSAP (black lines) and BAU (red lines) nutrient load scenarios respectively. Right: differences between the BSAP and BAU scenarios.