

Utrecht, July 17, 2015

Dear Prof. Fennel,

With this letter, we have uploaded our response to the two review reports of reviewers #6 and #7.

We hope that our manuscript can now be accepted for publication in BG.

We look forward to hearing from you.

Best regards,
Conny Lenz

Reply to reviewer #6

The authors investigated a very dynamic environment and one that is likely to yield great insights on the diagenetic behavior of manganese and the formation of manganese carbonates, an environment and topic to which I have given much thought. As such, this is a potentially very important contribution that will attract much attention among carbonate geochemists, diageneticists, and paleoceanographers. Hence, I read the manuscript with great interest.

The manuscript is clearly worthy of publication, but makes for very difficult reading because of the authors fail to properly describe the sedimentary environment, clearly state their working hypothesis and supporting evidence early on in the discussion. Instead the readers is kept guessing and many of the authors explanations initially appear as purely speculative. This being said, I believe that the manuscript could readily be modified to make it acceptable for publication.

Response. We have modified the introduction to directly bring forward a more extensive description of the sedimentary environment and bring forward all working hypotheses even more specifically as detailed further in our responses to comments 39-45.

Text moved from discussion to introduction and revised (page 3 line 18-32):
“Between inflows, when bottom waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are typically assumed to be undersaturated with respect to Mn carbonates down to a depth of ~5 to 8 cm based on saturation state calculations for idealized minerals (Carman and Rahm, 1997; Heiser et al., 2001). Mn oxides that formed during oxic inflows and settled in the surface sediment will dissolve upon subsequent exposure to reducing pore- or overlying water. This is thought to lead to high dissolved Mn concentrations in the pore water during – and shortly after – the inflow events. The high Mn concentrations in turn may lead to strong oversaturation with respect to Mn carbonates, although this has not been proven due to the lack of real-time studies during inflow events (Huckriede and Meischner, 1996; Sternbeck and Sohlenius, 1997, Heiser et al., 2001). Furthermore, high Mn concentrations must coincide with sufficiently high alkalinity for Mn carbonate precipitation to initiate (Lepland and Stevens, 1998). Despite these uncertainties, various authors have correlated historically-recorded inflow events to specific accumulations of Mn carbonate in sediments of the Gotland Basin (e.g. Heiser et al., 2001; Neumann et al., 1997).”

Detail comments follow.

1. As noted above, many of my comments (choice of sampling methodology, sediment and pore water extraction procedures, handling of sediment cores and analysis) and frustrations about this manuscript stem from the lack of information (e.g., physical and chemical characteristics of the sediment and limitations) provided by the authors in the text.

Response. We have extended the methods and results section as requested and as detailed below in our replies.

2. For example, is the porosity of the surface sediments really 99% as indicated in Table 3?

Response. Yes. Table 3 refers to Appendix B where the surface porosities for each site are listed and the value for the Gotland Basin is shown to be 99%.

3. If so, this explains why the authors can suck the sediment out of the cores, why the pore waters can easily be extracted by centrifugation, why the cores must embed their cores in resin prior to line scan analyses. The sediment porosities can be found in the appendices, but a one-sentence statement about this in the text would have eliminated much confusion.

That the sediments are fine-grained was noted at the start of the methods section, page 5, line 3. That the sediments are highly porous was stated in the results on page 12, line 13.

We now mention the highly porous nature of the sediment in the site description as well and mention the range of porosities in the surface sediments in the results.

New text (page 5, line 23): *"Fine-grained, highly porous sediments"*
(page 13, line 32f): *"Sediments are highly porous, with porosities in the surface sediment ranging from 87 to 99 vol% (Appendix B)."*

As described in the manuscript, two methods were used to collect porewater. In one case, syringes with the top cut-off were pushed into predrilled holes in the sediment and then removed. This does not involve "sucking". In the second case, sediment was sliced. In both cases the sediment was centrifuged to separate the porewater and sediment. Centrifugation is a well-established and widely used method for the collection of porewater from both fine grained and coarse grained sediments (with the type of centrifuge tube to be used depending on the grainsize).

4. Although fairly well written, the manuscript is long and makes for difficult reading.

Response. Our original manuscript was concise and to the point. In two previous rounds of revision, the original 13-page manuscript was expanded by 11 pages to address the wide range of comments of the previous 5 reviewers as requested by the various editors.

5. It is replete with grammatical errors, the abusive use of "However" at the beginning of sentences, the inappropriate use of "While" instead of "Whereas", and the awkward and frequent use of "in line" where 'consistent' would have been more appropriate. For the benefit of the authors, I have edited most of the manuscript and attach an annotated version to this review.

Response: We ask the reviewer to consider that we may have been taught to write in a different style. To avoid discussion, we have made most of the suggested changes in the annotated manuscript. The only exceptions were cases where this would lead to sentences that we consider to be grammatically incorrect (e.g. the suggested changes on p1, line 29, p4, line 20, p4 line 4) or where the meaning of the sentence would be altered (p5, line 17). We note that all BG manuscripts are edited for English in the final stages prior to publication.

Specific comments:

Abstract –

6. Page 1, lines 22-23: Where would this large pool originate from, if not from the accumulation of Mn diffusing out of the sediment?

Response: Indeed, the Mn has diffused out of the sediment previously. From the text, it should already have been clear that we were comparing present-day fluxes to the amount already present in the water column, because we were referring to “active release”. To avoid misunderstandings we now mention this:

Page 1. Line 20-23. Modified text in bold and underlined: “Although the **present-day** fluxes are significant (ranging up to ca. $240 \mu\text{mol m}^{-2} \text{d}^{-1}$), **comparison to** published water column data suggest that the **current** benthic release of Mn is small when compared to the large pool of Mn already present in the hypoxic and anoxic water column.”

7. Page 2, line 5: Why is the input of reactive Fe to these basins lower than in recent history? (Note that the authors eventually, late in the discussion, provide an explanation and, thus, keep the reader guessing, speculating, and questioning the authors’ interpretations until the end. This makes for a poor manuscript.)

Response: We now include an explanation for the changes in Fe input in the abstract as well:

Modified text (page 2, line 5-8): “Our data suggest that eutrophication has not only led to a recent rise in sulfate reduction rates but also to a decline in reactive Fe input to these basins. We hypothesize that these factors jointly have led to higher sulfide availability near the sediment-water interface after inflow events.”

Introduction –

8. Page 2, line 28: derived from sulfate reduction? (see comment above in parentheses)

Response: We have added “derived from sulfate reduction” to this sentence.

Materials and Methods –

9. Page 5, lines 19-20: Is this water truly representative of the bottom water as pore waters may be advected out of the sediment during corer penetration? This problem, which is normally neglected, is compounded by the small volume of overlying water recovered by the multi-corer.

Response. Multicorers have been specifically developed to allow the collection of intact sediment cores with overlying waters from the seafloor and are used by marine researchers worldwide in similar studies. Advection of porewater due to the corer penetration should be negligible as is evident from the sharp gradients in many porewater constituents in multicore sediment tubes obtained in this manner and the low concentrations of the same constituents in the bottom water.

10. Given the high porosity of the sediment, this is not likely a problem, but, as indicated above, the authors should let the reader know of the high sediment porosity instead of the reader having to seek out this information in the appendices.

Response: see our reply to comments 2 and 3 above.

11. Given the high sediment porosity, how was the sediment sampled with a multi-corer that cannot land/rest on a sediment surface? The only way I know to sample such high porosity sediment without disturbance is by a diver. Again, the authors need to add additional information.

Response: The multicorer could rest on the sediment by reducing the weights of the multicorer to a minimum and modifying the frame so that the multicorer did not rest on single legs but instead on a specially made circular device connecting the legs. Cores taken with a special corer for soft sediments (GEMAX; www.kolumbus.fi/boris.winterhalter/GEMAX.pdf) at the same sites showed identical solid phase profiles of chemical constituents.

Modified text (page 6, line 2-5): *"When sampling the sediment at these sites, the weights of the multicorer were reduced and frame of the multicorer was modified to prevent the frame from sinking into the soft sediment, allowing the retrieval of undisturbed sediment cores with overlying water"*

12. lines 21-22: Is the sediment porosity high enough that the sediment can be sucked out of the corer with a syringe? According to Table 3, sediment porosity is 99%! See previous comment.

Response: See our reply to comment 3. We have now added in the methods that we used cutoff syringes and provide additional details. Note that the data included in the Appendix show that the surface porosity is not equally high at all sites and decreases with depth.

Modified text (page 6, line 14-16): *"or sampled with syringes from which the top was cut-off and that were pushed into the sediment through taped, pre-drilled holes in the core liner. The tape was cut with a sharp object directly prior to inserting the syringe."*

13. Page 6, lines 12-13: This is a blanket statement that avoids doing a proper error analysis!

Response. We used this summary statement to keep the manuscript concise and to the point. We have now included details on the precision of each pore water analysis listed.

(page 6, line 23) *“The relative precision of the sulfide analyses determined for replicate samples was <10%.”*

(page 7, line 1) *“The relative precision of the NH₄⁺ analyses was <5%.”*

(page 7, line 4) *“The total alkalinity was then determined by titration with 0.01 M HCl with a precision of 0.05 meq/L.”*

14. , lines 18-19: How long and at what temperature were the bottles equilibrated? The authors assume that all the methane will have been salted-out in the presence of the saturated NaCl solution. Is the reader expected to guess this? At the very least, the authors should refer the reader to a paper where the analytical principle is laid out.

Response. We have added information on the reason for using a saturated NaCl solution including references.

Added text (page 7, line 13-22): *“The bottles were shaken and then stored upside down at room temperature for ca. 1 month before analysis in the laboratory at Utrecht. Selected samples were analysed again after one year and gave identical results. Methane was assumed to be quantitatively salted out into the headspace during the equilibration process. As determined by O’Sullivan and Smith (1970), methane is effectively insoluble in a NaCl solution of molality 4 at 100 atm pressure and 51 degC. In our case, the molality of the saturated salt solution was ~5, pressure was 1 atm and temperature 25 degC. As shown by the same authors, methane solubility declines with increasing salinity and decreasing pressure and is effectively independent of temperature, so our assumption of insolubility is valid. A similar method has been employed successfully by e.g. Mastalerz et al. (2009).”*

15. lines 27-28: Was the weight of residual sea-salts taken into consideration? Again, these data appear in the appendices, but the reader has to seek them out.

Response. This is not so. We refer the reviewer to line 9-10 on page 7 (now page 8 line 15-16) where this is explicitly mentioned in the main text of the methods section: *“All elemental concentrations in the sediment were corrected for the weight of the salt in the pore water using the ambient salinity and porosity”*.

16. lines 30-32: Was the TOC content normalized to the weight of the original sediment or to the decalcified sediment? Hopefully not the latter case since HCl will dissolve other phases than carbonates, including some of the OC.

Response. The TOC content was calculated as a percentage of the weight of the original sediment using the weight loss during decalcification. This is now explicitly mentioned in the text. We note that in most papers describing this

method, this information is not added. The loss of OC is very limited, as discussed in the reference we provided earlier.

Revised text (page 8, line 4-6): *“(Van Santvoort et al., 2002) where the measured TOC content in the decalcified sediment was converted to the content in the original sediment using the weight loss during decalcification.”*

17. Page 8, lines 1-3: Was the compression linear or did it vary with the porosity of the sample? What would be the impact of the latter on the age model based on the distribution of Mn and Mo? It would have helped the reader understand the choice of procedures if the authors had previously indicated that the sediment porosity was very high, as implied from Table 3 and indicated in the appendices.

Response: As stated on Page 8, Lines 23-25 (previous version of the manuscript), the LA-ICP-MS linescan data from the resin-embedded blocks was expanded to the original length of the core section, and subsequently aligned to discrete sample data for the same interval. We have expanded this section further, as detailed below.

Added text (page 9, line 1-7): *“Due to non-linear compaction of the sediments during the embedding procedure, the depth scale of the LA-ICP-MS data was adjusted by alignment to discrete sample data from the corresponding core section (not shown). Subsequently, fluctuations in Mo/Al and Mn/Al ratios were compared with instrumental records of bottom water oxygen conditions, and ages were assigned to features in the Mo/Al and Mn/Al profiles (see Appendix A, Fig. A2). The adjustment of the depth scale and the allocation of ages allowed sedimentation rates to be estimated (Appendix A; Fig. A3).”*

18. lines 19-22: Why not do XRF scanner analysis on the original core as is now often done. This would have avoided disturbance of the core (shrinkage) as a result of resin embedding? Again, it would have helped the reader understand the choice of procedures if the authors had previously indicated that the sediment porosity was very high, as implied from Table 3 and indicated in the appendices.

19. Response. The reviewer has already answered the question. XRF scanning cannot be done on these sediments without resin embedding because of their high porosity. The uppermost sections of the core cannot be laid horizontally (as required for XRF core scanning) without collapsing.

19, lines 28-29: Why not from the gradient across the sediment-water interface itself? The concentration gradient between 0.25 and 2.5 cm below the SWI is likely very different than the across the SWI. On the other hand, the authors probably meant between the overlying waters and pore waters concentrations at 0.25 or 2.5 cm depth. This would make more sense, but is not what is written.

Response. We are calculating the gradient *“over the upper 0.25 to 2.5 cm of the sediment”*, which in our understanding of the English language implies that we are referring to the zone from 0 to 0.25 to at maximum, 0 to 2.5 cm.

To avoid confusion, we have modified the text and now write (page 10, line 7-10): “...from the concentration gradient that was obtained from the difference in concentration in the bottom water and the first porewater sample (with the depths of this first sample ranging from 0.25 to 2.5 cm) using Fick’s first law for six sites”

20. Even so, depending on the thickness of the sediment oxic layer, the gradient between the OLW and 2.5 cm below the SWI may be very different than immediately across the SWI.

Response: We are aware that the actual gradient may be different, but at present there are no other techniques available to accurately measure gradients in dissolved Mn across the sediment-water interface and for the purpose of our study, this method is adequate.

21. Page 10, line 11: Should probably be second order and include alkalinity. Although manganese oxide reduction generates alkalinity, much more alkalinity is produced through sulfate reduction. The authors should assess if the first process generates sufficient alkalinity to trigger Mn carbonate precipitation

Response. As outlined in the text, the only purpose of the modeling is to demonstrate that changes in dissolved Mn availability near the sediment-water interface induced by changes in the availability of sulfide in the porewater have the potential to limit the precipitation of Mn carbonate in the surface sediments of the Baltic Sea. This was being debated by reviewer #1 and we prove with this model that our hypothesized mechanism is feasible.

By setting the rate constant for Mn carbonate formation at a high value, we assume from the start that sufficient alkalinity is generated in the sediment for the reaction to occur. This is a reasonable assumption when assessing the potential role of variations in dissolved Mn in the surface sediment.

The use of a first-order rate constant for a process that is more complex, does not imply that all other factors are ignored. Instead, it implies that all other factors are combined in the first-order rate constant (Berner, 1980) that we refer to in our manuscript. This textbook includes a specific example of the modeling of the precipitation of Mn carbonate in sediments as a first order process.

Note that the typical rate law used in reactive transport models is (Wang and Van Cappellen, 1996):

$$R = k_{prec}(\Omega - 1)$$

where Ω is the saturation state. When the carbonate concentration is high enough to allow for supersaturation with respect to Mn-carbonate formation (i.e. $\Omega > 1$) and alkalinity is constant, this rate law essentially behaves as a first order rate law with R depending on the dissolved Mn concentration. To

demonstrate this, we have plotted the rate (R; relative units) as a function of the Mn concentration for such a case below (Figure R1).

Added text (page 11, line 23-27). *“The use of a first-order rate constant for a process that is more complex, does not imply that all other factors are ignored. Instead, it implies that all other factors are combined in the first-order rate constant. This approach is outlined in detail in the textbook on diagenetic modeling by Berner (1980). Here, the dependence of the rate of Mn carbonate formation on only dissolved Mn implies that alkalinity is never limiting for Mn carbonate formation.”*

It would indeed be very interesting to include the processes leading to alkalinity generation and the saturation state of the porewater with respect to various possible Mn carbonate phases explicitly. For anyone with experience with diagenetic modeling, it should be evident that this requires another type of model (e.g. the model of Reed et al., 2011, expanded with carbonate chemistry), is a study in itself and therefore lies outside the scope of the present paper. We also note that such a detailed study would require field data for the sediment and porewater during and after an inflow. This is also why we state on Page 18, lines 20-22: *“Field studies of Mn dynamics in the water column and sediment during and directly after an inflow would be of particular value.”*

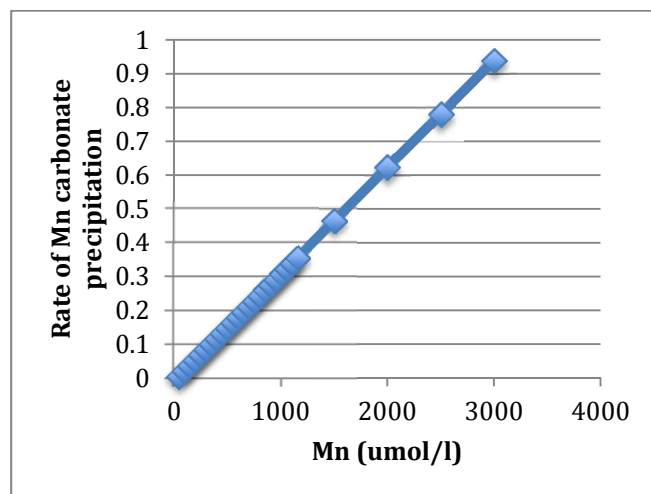


Figure R1. see reply to point 21.

22. , lines 22-24: What about the overlying waters, they must certainly serve as a boundary condition, as noted in Table 3.

Response. We do not understand the reviewer’s comment. The bottom water concentration of dissolved Mn is indeed the boundary condition at the sediment-water interface (i.e. at $x=0$) and our description of the model domain is consistent with the boundary condition in Table 3. For further details, we refer to the textbook by Berner (1980).

Results –

23. Page 11, line 19: The authors should refer to pore water Mn instead of Mn²⁺ if they suspect the presence of Mn(III), as their analytical protocol does not allow this distinction.

Response. We are aware of this issue and this is why we write the following on page 6, lines 4-6: "Total Mn and Fe are assumed to represent Mn²⁺ and Fe²⁺ although in the former case some Mn³⁺ may also be included". There is unlikely to be much Fe(III) in dissolved form in the environment that we are studying.

We also note that it is common to use this notation for porewaters – we refer to a myriad of other diagenetic studies such as that of Wang and Van Cappellen (2006; GCA) and for example that published by Pastor et al. (2011) in Biogeosciences.

To avoid further discussion, we have made the change. Because in our modeling and benthic flux calculations we specifically assume the presence of Mn²⁺, we must keep that notation in the text corresponding to those sections.

24., line 22: Same comment applies here as the authors' analytical protocol does not distinguish between dissolved Fe²⁺ and Fe(III).

Response: see above.

25. , line 24: If so, this means that there is little authigenic CaCO₃ precipitation and puts some constraints on the alkalinity (or [CO₃]) that can be reached in the pore water. On the other hand, the Mn enrichments are always well correlated with Ca enrichments (Figure 4).

Response. We do not understand the reviewer's point. We have measured the alkalinity, so there is no need to derive any constraints from the Ca profiles. Furthermore, at most sites, Mn-carbonate is thought to form directly following inflows. Thus, neither a decline in dissolved Ca with depth nor CaCO₃ formation would be expected at our time of sampling.

Discussion –

26. Page 14, line 14: Mn²⁺ is released to the pore water or the OLW, or both?

Response: We now state that we are referring to release to the overlying water (page 16, lines 12-13).

27, line 22: How can an undersaturation with respect to Mn carbonate develop under anoxic conditions when alkalinity is constantly being generated?

Response. Here, we are directly citing two earlier studies where undersaturation in surface sediments between inflows has been invoked to explain release of Mn to porewaters. There is no reason why alkalinity generation should naturally imply Mn carbonate formation. Our results in Figure 3 demonstrate this: at most sites, saturation indices for Mn carbonate indicate undersaturation in the upper layers of the sediment.

28. Page 16, lines 6-7: Does this mean that the dissolved Mn pool reached a steady state in 1.5 years?

Response. Yes, that's what we write in this sentence.

29. If so the benthic flux must, at first, have been much higher than the values stated above.

Response: Yes, indeed. That's what we wrote one page earlier, on page 15, line 25-26 (now page 17, line 21-22): "*Benthic fluxes of Mn are also expected to be high upon the reestablishment of bottom water anoxia after an inflow and then decline with time (Neretin et al., 2003).*"

30, lines 8-11: See previous comment.

Response: see previous reply.

31., lines 13-16: Unless the burial rate of Mn (in the form of carbonate or sulfide) has changed over time.

Response. The burial rate of Mn in the deep basins over recent decades has decreased as shown in Figure 4, which strengthens our statement here. We now include this in the text.

Added text (page 18, line 9f): "*... (Pohl and Hennings, 2005), and our observation that the burial of Mn has decreased at most sites (Figure 4),*"

32. line 17: These species (Mn²⁺), and particularly Mn(III), are not likely to be present as free ions in solution. Hence, it would be more appropriate to identify them as Mn(III) and Mn(II), respectively.

Response: We have implemented the suggested change.

33., Page 16, lines 30-31: Probably because the pool of Mn is dispersed/diluted in the water column. If so, the authors should specify it, instead of having it implied.

Response: Only Heiser et al. (2001) explain the undersaturation by resuspension linked to inflows and this is a hypothesis only, as discussed in the text on page 19. We have no evidence for such a resuspension and were not implying it here.

34. Page 17, line 17: It could not occur in diffusive contact with the undersaturated overlying water column, but could occur a few cm below the SWI in a more consolidated sediment.

Response: There is no reason why this could only occur a few cm below the SWI. This depends on the kinetics of the precipitation reaction relative to the rate of

diffusion. This is also demonstrated by the results of the diagenetic model which concentrates on the upper cm of the sediment only.

35. , lines 19-21: This conversion occurs stepwise and is relatively slow, probably on longer time scales than the formation of the Mn carbonates. The process is further limited by the diffusion of Mo from the overlying water column, although some might have been supplied by adsorption to Mn oxides settling to the sediment surface following the inflow of oxygenated waters.

Response: What the reviewer writes does not contradict what we write, given that an oxic period is required for the Mn oxide to deposit that ultimately will be converted rapidly to Mn carbonate. The Mo will then be incorporated in the sediments that are subsequently deposited under anoxic conditions. For further details on the Mo, see our replies to the earlier reviews.

36., line 25: Unlike Mo, the Fe usually originates from the sedimentary solid phases directly or following Fe(III) reduction by OM.

Response. In our setting, Fe(III) reduction by sulfide is expected to be more important. We did not mention the reductants to keep the text concise, but we have now expanded the text.

Revised text (page 19, line 11f): "Sulfur enrichments in sediments are typically associated with Fe-sulfides. These can form as the result of reduction of Fe(III) oxides with sulfide or organic matter (Boesen and Postma, 1988), and thus Fe sulfides can also be indicative of sulfidic conditions close to the sediment-water interface."

37., lines 26-28: This statement makes little sense as Mn(II) is unstable under oxic conditions. Perhaps the overlying water was oxic, but the environment in which the Mn carbonate precipitated must have been reducing to reduce the Mn(IV) oxides to Mn(II) and perhaps anoxic to provide the necessary alkalinity.

Response. To avoid confusion, we have changed this to (page 19, line 15f): *"relatively oxic conditions at the time of Mn deposition"*. As described earlier in the text, the Mn is deposited as Mn oxides under oxic conditions. The Mn oxides are subsequently reductively dissolved when anoxia sets in.

35. Page 18, line 4: in the Gotland Basin?

Response. We have changed *"of F80"* to *"in the Fårö Deep (F80)"*

36. lines 20-21: Could the MnS form at the expense of/or replacing the Mn carbonates?

Response: As indicated in the introduction, page 2, lines 28-29, formation of Mn-sulfides is expected when there is an excess of sulfide over Fe. It thus is unlikely that Mn sulfides will replace Mn carbonates.

Modified text (page 20, line 11f): *“These results could imply that increased rates of sulfate reduction linked to elevated inputs of organic material to the sediments drive the formation of Mn sulfide by contributing to an excess of sulfide over Fe.”*

37., lines 26-27: See previous comment.

see response to previous comment.

38. Page 19, lines 10-12: How else than following inflows would Mn-rich particles be supplied to the sediment at Landsort Deep? The authors leave too much unsaid, if they have an explanation.

Response. The explanation is already given one page earlier in lines 6-17 where we explain in detail that high inputs of Mn oxides and organic matter due to sediment focusing could explain why Mn sequestration in the Landsort Deep is not exclusively dependent on inflows. We now repeat this in the final part of this section.

Modified text (page 20, line 31f): *“This supports our hypothesis that the formation of Mn carbonate minerals in the Landsort Deep is not always related to inflows and that the Mn oxide supply is higher and more continuous when compared to other basins, due to much stronger sediment focusing related to the peculiar geometry.”*

39., line 30: What is responsible for these? From the previous text it would appear that the duration of the hypoxia and euxinia has increased between inflow events, but, as stated, it could also be interpreted as an increase in the strength of hypoxia (lower oxygen concentrations) or euxinia (higher sulfide concentrations). In the latter case, the authors should provide an explanation for this (e.g., increased influx of OM in response to eutrophication). (Again, the authors provide, later in the discussion, an explanation and, thus, keep the reader guessing, speculating, and questioning the authors' interpretations until the end. This makes for a poor manuscript.)

Response: In the introduction (page 3, lines 14-20) we already mention that both the hypoxic area and the euxinia have increased and that these are linked to eutrophication (which by definition implies a higher OM flux) and we provide relevant citations. We now have included in the text that this is implied by “eutrophication”.

Added text (page 4 line 1-4): *“Hydrographic data also indicate a major expansion of the hypoxic area in the Baltic Sea over the past century. This expansion is primarily caused by increased eutrophication, implying that the oxygen demand in deeper waters has increased as a result of a higher organic matter supply.”*

40. Page 20, paragraph 1: The evidence and scenario presented by the authors in this paragraph should have appeared earlier in the discussion instead of letting the reader guess what mechanisms are responsible for the increased reducing capacity of the deep basin sediments (increased flux of OM due to

eutrophication) and reduced shuttling of Fe to the deep basins (extension of hypoxic conditions to the shelves).

Response: see response to comment 39. Eutrophication as the cause of the hypoxia is mentioned in the introduction. Reduced shuttling of Mn to the deep basins is discussed in the introduction as well. The only topic that was not mentioned in the introduction was the reduced shuttling of Fe and we have now added this. We cannot bring up these issues earlier in the discussion given the changes we were asked to make by previous reviewers (e.g. discussion of the role of other reductants).

Revised text (page 5, line 3-6): *“A reduced shuttling of Fe oxides from shelves linked to expanding hypoxia (e.g. Lyons and Severmann, 2006) could contribute to this mechanism by reducing the buffering capacity of the sediments for sulfide (Diaz and Rosenberg, 2008).”*

41. Page 20, line 4: The authors are skipping several steps and should add: ... the accumulation of Mn oxides at the sediment-water interface, and the re-establishment of reducing conditions, ...

Response: We have rephrased the text as follows (page 21 line 22-29): *“The formation of Mn carbonates in Baltic Sea sediments is typically believed to be induced by the high alkalinity linked to organic matter degradation combined with high dissolved Mn concentrations in the surface sediment. These high dissolved Mn concentrations are thought to be the result of reductive dissolution of Mn oxides that have formed at the sediment-water interface directly following an inflow of oxygenated North Sea water. When anoxia is re-established and they are dissolved (Lepland and Stevens, 1998), supersaturation with respect to Mn carbonates is assumed to be reached in the surface sediment and not only at depths below ca. 5-10 cm (Figure 3).”*

42, lines 10-11: Why? Increases sulfate reduction? (see comment above in parentheses)

Response: This is unknown at present and is not specifically addressed in the cited paper. Since submission of our manuscript to BG, a paper has been published that discusses the various options for this rise in alkalinity but does not reach a conclusive answer (Gustafsson et al., 2014; Global Biogeochemical Cycles, 10.1002/2014GB004888). In our manuscript, the fact that it has increased is most important, because it shows that the lack of Mn carbonate formation cannot be explained by changes in alkalinity.

We now include a reference to the paper of Gustafsson et al. (2014) and write (page 22, line 2f): *“possibly due to higher rates of anaerobic mineralization linked to eutrophication (Gustafsson et al., 2014).”*

43. line 16: Why? Faster onset of hypoxia and euxinia due to greater influx of OM? (see comment above in parentheses)

Response: See reply to comment 40.

44., lines 28-30: This argument could have been brought forward earlier in the discussion.

Response: It is now introduced explicitly in the introduction. Note that in the earlier reviews we were asked to discuss the other reductants and all the other options. This has led to the current structure of this section.

45. Page 21, lines 4-6: Again, this argument should have been raised earlier, instead of letting the reader guess.

Response: Moved to the introduction.

Conclusions –

46. Page 22, line 28: It would be more logical to invert these statements as the loss of Mn²⁺ inhibits the formation of carbonates.

Response. We have made the suggested change.

Other comments-

47. What of the role of AVS and their strong affinity for Mn(II)? The adsorption of Mn(II) to AVS can control the porewater Mn(II) concentrations and the conversion of AVS to pyrite could provide a deep source of Mn(II).

Response: We have no data on AVS for these sites. To our knowledge the only published AVS data for the Gotland Deep are those of Boesen and Postma (1988). They found that practically all Fe-sulfide in the sediment was present as pyrite. Given the lack of additional data, it would be pure speculation to include a discussion of these processes.

48. (Morse and Luther (1999) mention that Mn(II) can also be pyritized?)

Response: We specifically address the role of pyrite in the introduction (page 2, lines 29-32) where we write: *“Some Mn may also be incorporated in pyrite (e.g Huerta-Diaz and Morse, 1992; Jacobs et al., 1985) but the amounts are relatively minor when compared to those present in Mn carbonate, as shown in a recent study for Baltic Sea sediments (Lenz et al., 2014).”*

49. One would think that they (Mn and Mo enrichments) might be related since molybdate adsorbs strongly onto Mn oxides and could be scavenged from the water column as Mn oxides settle out, unless the adsorption kinetics is slow and significant concentrations can only be obtained through diagenetic recycling across the oxic-suboxic boundary.

Response. As can be seen in Figure 4, sediment Mo and Mn are not related in the upper part of the sediment at the Faro and Gotland deep sites. This is why we discussed this mismatch explicitly in the original and first revised version of the

manuscript and wrote *“In the Fårö and Gotland Deep sediments, recent Mo enrichments go hand in hand with Mn depletions and permanent euxinia in bottom waters (Figure 6). Given that sinking Mn oxide particles do not survive downward transport through a sulfidic water column (Dellwig et al., 2010), these results further imply that sinking Mn oxides are, at present, likely not the main carrier of Mo to the sediment in the Baltic Sea.”*

This sparked such a debate with reviewers #2 and #3 that we removed this section from the paper, as suggested as an option by reviewer #2. Notably, reviewer #5 fully agreed with our interpretation (for further details, we refer to our replies following the first and second revision of this manuscript).

50. How does the record of inflows over the past two decades compare to previous decades in terms of frequency and intensity?

Response: The frequency of inflows has declined. We now explicitly mention this in the introduction.

Added text (page 3, line 16-18): *“Since the end of the 1970’s, the frequency of North Sea inflows has declined from multiple events per decade to only one inflow per decade (e.g. Mohrholz et al., 2015).”*

51. Supersaturation of surface sediment pore waters following an inflow event is unlikely, if there is a finite oxic zone (as long as there is dissolved oxygen in the overlying waters since the production of metabolic CO₂ will lower pH. What makes it supersaturated at depth? The accumulation of carbonate alkalinity from sulfate reduction?

Response: Both the rise in dissolved Mn and alkalinity contribute to the supersaturation at depth. We do not see what change the reviewer is suggesting here.

Reply to reviewer # 7

Review comments

Lenz et al. looks at how expanding hypoxia may influence Mn burial in the Baltic Sea. They present a detailed data set of porewater and sediment geochemistry for sites that range from fully oxic to euxinic which, even on its own, represents a significant contribution to the field. The authors, suggest that recent inflow events of oxic waters to the Gotland deep basin of the Baltic are no longer being recorded in the Mn-carbonate record. They proposed a mechanism for this change, whereby recent eutrophication of the Baltic has stimulated sulfide production in the sediments, and this sulfide production prevents Mn-carbonates from forming. The authors proposed mechanism is speculative, however they do present a diagenetic model that demonstrates, at least in theory, that this mechanism is possible.

As is evident by the reviews of this manuscript, this interpretation is contentious, however due to the importance of this issue with regards to using Mn-carbonates as a proxy for redox state, I think this is a debate that would be best settled in the literature, where they and others can test and eventually verify or disprove this hypothesis. For this reason I recommend publication, provided that the following comments are addressed.

Response. We are again surprised that our interpretation is seen as contentious by this reviewer but are happy to hear that this reviewer supports publication of our manuscript. As stated in our manuscript (page 22, lines 22-24) and in our previous replies, our findings are consistent with the general interpretation of sediment records of Mn in paleoceanography and the use of Mn as a redox proxy, where absence of Mn carbonates in sediments is assumed to be indicative of euxinic bottom waters (e.g. Calvert and Pedersen, 1993).

Major Comments

1) The addition of the diagenetic model is an improvement to the manuscript, as it provides a demonstration that the hypothesized Mn dynamics at the Gotland Deep site are possible, and makes their argument for this mechanism much more convincing. However I think they could do a better job of explaining the model results. For example I found figure 6C very confusing. It is strange to plot each form of magnesium (Mn^{2+} , Mn-oxides Mn-carbonates) at a different time in the simulation, and on a first read I had no idea what this figure was trying to show. It would be better to show a time series of how each Mn species changed throughout the simulation. For example plots of the depth integrated Mn^{2+} , Mn-oxides, Mn-carbonates over time would be far more intuitive for readers and, I think, demonstrate their point far more clearly.

Response. Although we prefer the original presentation of the results because it is more concise, we have replaced Figures 6A and 6B by two new panels (new Figures 6A, B) showing the temporal change of the Mn oxides and Mn carbonates in the sediment as suggested by the reviewer. We have also modified the corresponding text. The temporal trends in the dissolved Mn and benthic fluxes are now included in Appendix C.

Revised text (page 15, line 7-19): *“The change in the integrated amount of Mn oxide and Mn carbonate in the sediment with time as calculated with the diagenetic model, depends on the value of the rate constant for the reduction of Mn oxides (k_{red}) assumed for the period with oxic (4 months) bottom waters (Figures 6A and B). The amount of Mn oxide that is preserved during this phase decreases with increasing values of k_{red} . When k_{red} is low, most of the Mn oxide deposited on the sediment is preserved during the first 4 months of the simulation. The results show that the more Mn oxide is preserved during the oxic phase, the more Mn carbonate forms during the following anoxic phase because less dissolved Mn escapes to the overlying water through diffusion. In runs with low values of k_{red} , Mn carbonate is mostly formed in the 2-month anoxic phase. At intermediate values of k_{red} , there is also formation of Mn carbonate in the oxic phase. At high values of k_{red} , Mn carbonate formation is negligible. Corresponding changes in integrated*

amounts of dissolved Mn in the sediment and benthic fluxes of Mn during the simulations are shown in Appendix C.” “

At the very least the time points where the depth profiles are taken from must be more clearly labeled on the figure. In the figure caption they say “Depth profiles of Mn oxide (after 4 months), Mn²⁺ at the start of the anoxic phase” does this mean the Mn²⁺ profile are at the same point in time as the Mn oxide profile, if not at what timepoint in the simulation is it taken from? “...at the start of the anoxic phase..” is vague.

Response: We have labeled the time points in the figure as suggested. The profile of dissolved Mn at the start of the anoxic phase is for 4 months and 8 hours. We wish to keep this figure because it demonstrates the contrast between the behaviour of the three key forms of Mn in the three key phases of the scenario (oxic phase where Mn oxide is crucial, start of anoxic phase where Mn is released and at the end when all the Mn carbonate has accumulated). It also demonstrates that the MnCO₃ profiles compare well to the values found in Figure 4.

Revised caption: *Figure 6. A. Integrated amount of Mn oxide and B: Integrated amount of Mn carbonate in the upper cm of the sediment (in mol m⁻²) for the simulations with k_{red} being equal to either 0.1, 1, 10, 100 or 1000 yr⁻¹ for the first 4 months and equal to 1000 yr⁻¹ for the last 2 months, as described in the text. C: Depth profiles of Mn-oxide (after 4 months, end of oxic phase), dissolved Mn (after 4 months and 8 hours, directly after the start of the anoxic phase) and MnCO₃ (after 6 months) as calculated with the model in the same scenarios as A and B.”*

Revised text (page 15, line 20-27): *“Examples of depth profiles of Mn oxides, dissolved Mn and Mn carbonate at various key stages of the simulation illustrate the dependence of Mn carbonate formation on the rate of reduction of Mn oxides during the oxic phase (Figure 6C). After 4 months, a large amount of Mn oxides has accumulated in the surface sediment when k_{red} is equal to 0.1 yr⁻¹. Such an enrichment is absent when k_{red} is 1000 yr⁻¹. High dissolved Mn concentrations at the onset of the anoxic phase (shown for 4 months and 8 hours) and the formation of a Mn carbonate-rich layer (shown for the end of the simulation) is restricted to the scenario which allows the Mn oxides to accumulate.”*

2) The Mn²⁺ depth profile in Figure 6C has magnesium concentrations well above anything observed in Figure 2 (and an order of magnitude above what is observed in Gotland Deep). Also is a concentration of 16000 $\mu\text{mol/g}$ of Mn oxide reasonable, by my calculation this would work out to a Mn[%wt] of 86% [(0.016 mole * 54g/mole)/1 g sed x 100 = 86%]. I think the model results would be more believable if their parameter choices produced concentrations that were at least the same order of magnitude as what they observe.

Response: We are modeling conditions in the surface sediment directly following an inflow and there are no field data for sediment Mn oxide and porewater Mn following such an inflow to compare to - our data refer to conditions, several years after an inflow. The numbers we refer to are realistic and are in line with

the scenario outlined in section 4.1 as referred to in Table 3 where the boundary condition for the simulation is explained. Briefly, we assume that the Mn that is present in the water column sinks down to the surface of the sediment in a period of 4 months. The Mn-carbonate layer that subsequently forms in the sediment in the model is of the right order of magnitude and is in accordance with the reported values of ca. 1 wt% of Mn in Figure 4.

3) I think the model is under utilized in the manuscript. By looking at the Damkohler numbers for each transport process and rate constant, I think it is likely that the authors could do a better job of characterizing the tipping point between Mn-carbonate preservation and preservation, these would help make their conclusions more quantitative.

Response: Damkohler numbers are typically used to look at one reaction and one transport process. Here, there are two relevant reactions and one transport process. We don't see how this can be captured in a Damkohler number.

4) a) I am concerned by the fact that the model does not treat Mn-carbonate formation as a precipitation/dissolution reaction that accounts for thermodynamic equilibrium.

Response: For further details on the model approach and justification of the rate law used, we refer to our response to reviewer #6, comment 21 and the textbook by Berner (1980).

4) b) This despite the fact that as Figure 3 shows sediment conditions transition with depth from under to over saturation at most sites. I am wondering if the lack of Mn-carbonate preservation in Gotland Deep could not also be explained simply by changes in saturation state between oxic and anoxic conditions.

Response: We do not understand this comment. We are concentrating on the upper cm of the sediment in the model. Figure 3 shows that porewaters in this zone of the sediment are anoxic and undersaturated with respect to Mn carbonate in between inflows – the time of our sampling. This will not change when the sediment becomes oxic directly following an inflow because any Mn will be in the form of Mn oxides. Supersaturation with respect to Mn carbonate is only reached when anoxia returns after an oxic period because of the dissolution of the massive amount of Mn oxides that can settle from the water column. The key issue here is that this used to lead to Mn carbonate formation but over the past decade this no longer occurs. All of this is explained in the text.

Minor comments

- 1) The authors should say what the initial conditions for their model simulations were.

Response: Added, as suggested.

Modified text (page 12, line 14-16): *“We assume that there is no Mn in the sediment (in any form) at the start of the scenario, consistent with Mn being low or*

absent in surface sediments in the Gotland basin between inflows (Figure 4).“

- 2) Page 18-line 6 (> 1 μM verses <0.26 mM Mn^{2+}) should be (> 1 mM verses <0.26 mM Mn^{2+})

Response: the typo has been corrected.

1 **Are recent changes in sediment manganese sequestration**
2 **in the euxinic basins of the Baltic Sea linked to the**
3 **expansion of hypoxia?**

4

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12

13 **Abstract**

14 Expanding hypoxia in the Baltic Sea over the past century has led to the development of
15 anoxic and sulfidic (euxinic) deep basins that are only periodically ventilated by inflows of
16 oxygenated waters from the North Sea. In this study, we investigate the potential
17 consequences of the expanding hypoxia for manganese (Mn) burial in the Baltic Sea using a
18 combination of pore water and sediment analyses of dated sediment cores from 8 locations.
19 Diffusive fluxes of dissolved Mn from sediments to overlying waters at oxic, hypoxic and
20 euxinic sites are consistent with an active release of Mn from these areas. Although the
21 present-day fluxes are significant (ranging up to ca. 240 $\mu\text{mol m}^{-2} \text{d}^{-1}$), comparison to
22 published water column data suggests that the current benthic release of Mn is small when
23 compared to the large pool of Mn already present in the hypoxic and anoxic water column.
24 Our results highlight two modes of Mn carbonate formation in sediments of the deep basins.
25 In the Gotland Deep area, Mn carbonates likely form from Mn oxides that are precipitated
26 from the water column directly following North Sea inflows. In the Landsort Deep, in
27 contrast, Mn carbonate and Mn sulfide layers appear to form independently of inflow events,
28 and are possibly related to the much larger and continuous input of Mn oxides linked to
29 sediment focusing. Whereas Mn-enriched sediments continue to accumulate in the Landsort

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1 | Deep, this does not hold for the Gotland Deep area. Here, a recent increase in euxinia, as
2 | evident from measured bottom water sulfide concentrations and elevated sediment
3 | molybdenum (Mo), coincides with a decline in sediment Mn content. Sediment analyses also
4 | reveal that recent inflows of oxygenated water (since ca. 1995) are no longer consistently
5 | recorded as Mn carbonate layers. Our data suggest that eutrophication has not only led to a
6 | recent rise in sulfate reduction rates but also to a decline in reactive Fe input to these basins.
7 | We hypothesize that these factors jointly have led to higher sulfide availability near the
8 | sediment-water interface after inflow events. As a consequence, the Mn oxides may be
9 | reductively dissolved more rapidly than in the past and Mn carbonates may no longer form.
10 | Using a simple diagenetic model for Mn dynamics in the surface sediment, we demonstrate
11 | that an enhancement of the rate of reduction of Mn oxides is consistent with such a scenario.
12 | Our results have important implications for the use of Mn carbonate enrichments as a redox
13 | proxy in marine systems.

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15 | 1 Introduction

16 | Manganese (Mn) enrichments in brackish and marine sedimentary deposits can be used as an
17 | indicator of redox changes in the overlying waters (e.g. Calvert and Pedersen, 1993). In
18 | anoxic settings, Mn-enrichments are typically assumed to consist of Mn carbonates, which are
19 | associated with calcium and can contain other impurities (e.g. Jakobsen and Postma, 1989;
20 | Manheim, 1961; Sternbeck and Sohlenius, 1997; Suess, 1979). For simplicity, in this study
21 | these phases are collectively referred to as Mn carbonates, despite their obvious greater
22 | complexity and heterogeneity. Mn carbonate minerals are suggested to form from Mn oxides
23 | deposited during periods of bottom water oxygenation (Calvert and Pedersen, 1996;
24 | Huckriede and Meischner, 1996), with dissolved Mn availability thought to be the key control
25 | (Neumann et al., 2002). Nevertheless, sediment Mn data for both the Landsort Deep in the
26 | Baltic Sea (Lepland and Stevens, 1998) and the Black Sea (Lyons and Severmann, 2006)
27 | indicate that Mn enrichments may also form in sediments overlain by continuously anoxic
28 | bottom waters. In the Landsort Deep, these enrichments consist of both Mn carbonates and
29 | Mn sulfides (Lepland and Stevens, 1998; Suess, 1979). The formation of Mn carbonate is
30 | assumed to be driven by an exceptionally high alkalinity derived from sulfate reduction,
31 | whereas Mn sulfides form when H₂S exceeds Fe availability (Böttcher and Huckriede, 1997;
32 | Lepland and Stevens, 1998). Some Mn may also be incorporated in pyrite (e.g. Huerta-Diaz

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1 and Morse, 1992; Jacobs et al., 1985), but the amounts are relatively minor when compared to
2 those present in Mn carbonate, as shown in a recent study for Baltic Sea sediments (Lenz et
3 al., 2014). Finally, Mn enrichments may also form in sediments overlain by oxic bottom
4 waters upon increased input and precipitation of Mn oxides and transformation to Mn
5 carbonate during burial (e.g. Macdonald and Gobeil, 2012). A better understanding of the
6 various modes of formation of sedimentary Mn and the link with variations in bottom water
7 redox conditions is essential when interpreting Mn enrichments in geological deposits (e.g.
8 Calvert and Pedersen, 1996; Huckriede and Meischner, 1996; Jones et al., 2011; Meister et
9 al., 2009).

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10 Redox-dependent dynamics of Mn have been studied extensively in the Baltic Sea (e.g.
11 Huckriede and Meischner, 1996; Lepland and Stevens, 1998; Neumann et al., 2002) and are
12 of interest because of the large spatial and temporal variations in bottom water oxygen
13 conditions over the past century that are particularly well documented since the 1970's
14 (Fonselius and Valderrama, 2003). The available hydrographic data provide evidence for
15 sporadic inflows of oxygenated saline water from the North Sea that affect brackish bottom
16 waters in all deep basins (Matthäus and Franck, 1992; Matthäus et al. 2008). Since the end of
17 the 1970's, the frequency of North Sea inflows has declined from multiple events per decade
18 to only one inflow per decade (e.g. Mohrholz et al., 2015). Between inflows, when bottom
19 waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are
20 typically assumed to be undersaturated with respect to Mn carbonates down to a depth of ~5
21 to 8 cm based on saturation state calculations for idealized minerals (Carman and Rahm,
22 1997; Heiser et al., 2001). Mn oxides that formed during oxic inflows and settled in the
23 surface sediment will dissolve upon subsequent exposure to reducing pore- or overlying
24 water. This is thought to lead to high dissolved Mn concentrations in the pore water during –
25 and shortly after – the inflow events. The high Mn concentrations in turn may lead to strong
26 oversaturation with respect to Mn carbonates, although this has not been proven due to the
27 lack of real-time studies during inflow events (Huckriede and Meischner, 1996; Sternbeck
28 and Sohlenius, 1997, Heiser et al., 2001). Furthermore, high Mn concentrations must coincide
29 with sufficiently high alkalinity for Mn carbonate precipitation to initiate (Lepland and
30 Stevens, 1998). Despite these uncertainties, various authors have correlated historically-
31 recorded inflow events to specific accumulations of Mn carbonate in sediments of the Gotland
32 Basin (e.g. Heiser et al., 2001; Neumann et al., 1997).

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1 Hydrographic data also indicate a major expansion of the hypoxic area in the Baltic Sea over
2 the past century. This expansion is primarily caused by increased eutrophication, implying
3 that the oxygen demand in deeper waters has increased as a result of higher organic matter
4 supply (Carstensen et al., 2014; Conley et al., 2009; Gustafsson et al., 2012; Savchuk et al.,
5 2008). While the shallower areas in the Baltic Sea are now seasonally hypoxic, the deep
6 basins all show a major shift towards anoxic and sulfidic (euxinic) conditions around 1980
7 (Fonselius and Valderrama, 2003; Mort et al., 2010). These basin-wide changes in redox
8 conditions likely had a major impact on both the sources and sinks of sediment Mn in the
9 Baltic Sea.

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10 River input (Ahl, 1977; Martin and Meybeck, 1979) and release from sediments (Sundby et
11 al., 1981; Yeats et al., 1979) are the key sources of Mn in the water column of marine coastal
12 basins. Whereas in areas with oxic bottom waters, dissolved Mn produced in the sediment
13 will mostly be oxidized to Mn oxide in the surface layer and thus will be trapped in the
14 sediment, dissolved Mn may escape to the overlying water when the oxic surface layer is very
15 thin (Slomp et al., 1997). In the water column, this Mn may be oxidized again (e.g. Dellwig et
16 al., 2010; Turnewitsch and Pohl, 2010) and contribute to the depositional flux of Mn oxides
17 (Mouret et al., 2009), or may be laterally transferred in dissolved or particulate form. The
18 lateral transfer of Mn from oxic shelves to deep basins, where the Mn may be trapped and
19 ultimately may precipitate as authigenic minerals, is termed the “Mn shuttle” (Lyons and
20 Severmann, 2006).

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21 During the expansion of hypoxia and anoxia, as observed in the Baltic Sea over the past
22 century (Conley et al., 2009), the Mn shuttle likely became more efficient in transporting Mn
23 to deeper, euxinic basins because of decreased trapping of Mn in oxygenated surface
24 sediments (Lyons and Severmann, 2006). However, during an extended period of hypoxia and
25 anoxia, sediments in hypoxic areas may become depleted of Mn oxides, thus reducing the
26 strength of the Mn shuttle from oxic and hypoxic shelves to the deep basins. In addition, the
27 formation rate of authigenic Mn minerals in deep basin sediments may change in response to
28 bottom water hypoxia and anoxia. If release of dissolved Mn²⁺ from Mn oxides – formed at
29 the sediment surface following inflows of oxygenated North Sea water – is the dominant
30 control for Mn carbonate formation in the sediment as suggested for the Gotland Deep
31 (Neumann et al., 2002), expanding bottom water anoxia might allow Mn oxides to be reduced
32 by sulfides in the anoxic and sulfidic water column and at the sediment-water interface,

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1 precluding conversion to Mn carbonates. This mechanism was recently invoked to explain the
2 lack of Mn carbonates in the sediment during periods of bottom water euxinia in the Gotland
3 Deep during the Holocene Thermal Maximum (Lenz et al., 2014). A reduced shuttling of Fe
4 oxides from shelves linked to expanding hypoxia (e.g. Lyons and Severmann, 2006) could
5 contribute to this mechanism by reducing the buffering capacity of the sediments for sulfide
6 (Diaz and Rosenberg, 2008). If alkalinity production is the key control, however, as suggested
7 for the Landsort Deep (Lepland and Stevens, 1998), Mn sequestration would be expected to
8 be similar or increase due to higher rates of sulfate reduction.

9 In this study, we use geochemical analyses of dated sediment cores for 8 sites in the Baltic
10 Sea, combined with pore water data to assess the role of variations in water column redox
11 conditions for Mn dynamics in surface sediments in the Baltic Sea. We capture the full range
12 of redox conditions (oxic, hypoxic and euxinic) to investigate the cycling of Mn in the
13 sediment, the present-day diffusive flux from the sediments and the sequestration of Mn in
14 mineral phases. Whereas the pore water data only provide a “snapshot” of the conditions at
15 the time of sampling, the sediment data in the euxinic basins record both the expansion of
16 hypoxia and anoxia and the effects of short-term inflows of oxygenated North Sea water. Our
17 results indicate release of Mn from oxic and hypoxic areas as well as the deep basin sites, and
18 sequestration of Mn carbonates and sulfides in the Landsort Deep. The lack of recent Mn
19 accumulation at various deep basin sites suggests that inflows of oxygenated seawater are no
20 longer consistently recorded by Mn carbonate deposits in these settings.

21 **2 Materials and Methods**

22 **2.1 Study area**

23 Fine-grained, highly porous sediments from 8 locations in the southern and central Baltic Sea
24 were collected during 4 cruises between 2007 and 2011 (Figure 1, Table 1) using a multi-
25 corer. The sites differ with respect to their water depths and their present-day bottom water
26 redox conditions. The Fladen and LF1 sites are located in the Kattegat and along the eastern
27 side of the Gotland Deep, respectively, and are fully oxic, whereas site BY5 in the Bornholm
28 Basin is seasonally hypoxic (Jilbert et al., 2011; Mort et al., 2010). The remaining stations,
29 LF3, LL19, BY15 (Gotland Basin), F80 (Fårö Deep) and LD1 (Landsort Deep), are situated
30 below the redoxcline, which was located between 80 and 120 m water depth at the time of
31 sampling. Therefore, bottom waters at these sites were all anoxic and sulfidic (euxinic). The

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1 latter 4 sites are located in the deep central basins of the Baltic Sea, at water depths ranging
2 from 169 m at LL19 to 416 m at LD1. When sampling the sediment at these sites, the weights
3 of the multicorer were reduced and the frame of the multicorer was modified to prevent it
4 from sinking into the soft sediment, allowing the retrieval of undisturbed sediment cores with
5 overlying water. Water column data for oxygen and hydrogen sulfide for LL19 and LD1 (as
6 recorded at LL23 as a nearby station) are available from the ICES Dataset on Ocean
7 Hydrology (2014). The sampling, as well as selected pore water and sediment analyses for
8 many of our sites have been described previously (Mort et al., 2010, Jilbert et al., 2011; Jilbert
9 and Slomp, 2013a). For completeness, all procedures are described below.

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10 **2.2 Bottom water and pore water analyses**

11 A bottom water sample was taken from the water overlying the sediment in each multicore as
12 soon as possible after core collection. At each site, sediment multi-cores (<50 cm, 10 cm i.d.)
13 were either immediately sectioned in a N₂-filled glovebox at in-situ temperature or sampled
14 with syringes from which the top was cut-off and that were pushed into the sediment through
15 taped, pre-drilled holes in the core liner. The tape was cut with a sharp object directly prior to
16 inserting the syringe. A small portion of each sample was stored at 5°C or -20°C in gas-tight
17 jars for sediment analyses. The remaining sediment was centrifuged (10-30 min.; 2500 g) in
18 50 ml Greiner tubes to collect pore water. Both the pore water and a bottom water sample
19 were filtered (0.45 µm pore size) and subdivided for later laboratory analyses. All pore water
20 handling prior to storage was performed in a N₂ atmosphere. A subsample of 0.5 ml was
21 directly transferred to a vial with 2 ml of a 2% Zn-acetate solution for analysis of hydrogen
22 sulfide. Sulfide concentrations were determined by complexation of the ZnS precipitate using
23 phenylenediamine and ferric chloride (Strickland and Parsons, 1972). The relative precision
24 of the sulfide analyses determined for replicate samples was <10%. Subsamples for total Mn,
25 Fe, Ca and S were acidified with either HNO₃ (Fladen, BY5) or HCl (all other stations) and
26 stored at 5°C until further analysis by Inductively Coupled Plasma – Optical Emission
27 Spectroscopy (ICP-OES; Perkin Elmer Optima 3000; relative precision and accuracy as
28 established by standards (ISE-921) and duplicates were always <5%). Hydrogen sulfide was
29 assumed to be released during the initial acidification, thus S is assumed to represent SO₄²⁻
30 only. Total Mn and Fe are assumed to represent Mn²⁺ and Fe²⁺ although in the former case
31 some Mn³⁺ may also be included (Madison et al., 2011). Subsamples for NH₄ were frozen at -
32 20°C until spectrophotometric analysis using the phenol hypochlorite method (Riley, 1953).

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1 The relative precision of the NH₄⁺ analyses was <5%. A final subsample was used to
2 determine the pH with a pH electrode and meter (Sentron). We note that degassing of CO₂
3 may impact ex-situ pH measurements leading to a rise in pH (Cai and Reimers, 1993). Hence,
4 our reported pH values should be considered as approximate. The total alkalinity was then
5 determined by titration with 0.01 M HCl with a precision of 0.05 meq/L. All colorimetric
6 analyses were performed with a Shimadzu spectrophotometer.

7 At four deep basin sites (LL19, BY15, F80, LD1), a second multicore was sampled and
8 analysed for methane as described by Jilbert and Slomp (2013a). Briefly, a cutoff syringe was
9 inserted into a pre-drilled, taped hole at 1.5 cm intervals directly after core collection.
10 Precisely 10 ml wet sediment was extracted from each hole and transferred immediately to a
11 65 ml glass bottle filled with a saturated sodium chloride (NaCl) solution. This bottle was
12 then closed with a rubber stopper and screwcap, and a headspace of 10 ml N₂ gas was
13 inserted. The bottles were shaken and then stored upside down at room temperature for ca. 1
14 month before analysis in the laboratory at Utrecht. Selected samples were analysed again after
15 one year and gave identical results. Methane was assumed to be quantitatively salted out into
16 the headspace during the equilibration process. As determined by O'Sullivan and Smith
17 (1970), methane is effectively insoluble in a NaCl solution of molality 4 at 100 atmosphere
18 pressure and 51 degrees Celsius. In our case, the molality of the saturated salt solution was
19 ~5, pressure was 1 atmosphere and temperature 25 degrees Celsius. As shown by the same
20 authors, methane solubility declines with increasing salinity and decreasing pressure and is
21 effectively independent of temperature, so our assumption of insolubility is valid. A similar
22 method has been employed successfully by e.g. Mastalerz et al. (2009). Methane
23 concentrations in the headspace of the glass bottles were determined by injection of a
24 subsample into a Thermo Finnigan Trace GC gas chromatograph (flame ionization detector,
25 Restek Q-PLOT column of 30 m length, 0.32 mm internal diameter, oven temperature 25°C).
26 Data were then back-calculated to the original pore water concentrations using the measured
27 porosities (see Section 2.3). Because of degassing, which is unavoidable at sites with very
28 high CH₄ concentrations, the CH₄ profile at LD1 is expected to have a larger error than at
29 other sites, and likely represents a minimum estimate of the true concentrations.

30 **2.3 Sediment analyses**

31 Sediment samples were freeze-dried and water contents and porosities were calculated from
32 the weight loss, assuming a sediment density of 2.65 g cm⁻³. Sediments were then ground in

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1 an agate mortar in a N₂ or argon-filled glovebox. From each sediment sample, aliquots for
2 several different analyses were taken. For total organic carbon (TOC) analyses, 0.3 g of
3 sediment was decalcified with 1M HCl and the C content was determined with a Fisons NA
4 1500 CNS analyser (van Santvoort et al., 2002) whereafter the measured TOC content in the
5 decalcified sediment was converted to the content in the original sediment using the weight
6 loss during decalcification. Based on the analyses of laboratory reference materials and
7 replicates, the relative error of the TOC measurements was generally less than 5%. Total
8 sediment contents of S, Mn, Ca, Fe, Al and Mo were determined by ICP-OES, after
9 dissolution of 0.125 g of sample with an HF/HClO₄/HNO₃ mixture in closed Teflon bombs at
10 90°C, followed by evaporation of the solution and redissolution of the remaining gel in 1M
11 HNO₃ (Passier et al., 1999). The accuracy and precision of the measurements were
12 established by measuring laboratory reference materials (ISE-921 and in-house standards) and
13 sample replicates; relative errors were <5% for all reported elements. The detection limits of
14 ICP-OES for Mn, Mo, Ca, Fe, Al and S in the HNO₃ solution are 0.6, 14, 5, 6 and 24 µg kg⁻¹
15 and 0.28 mg kg⁻¹ respectively. All elemental concentrations in the sediment were corrected for
16 the weight of the salt in the pore water using the ambient salinity and porosity.

17 Age models based on ²¹⁰Pb analyses for 6 multi-cores used in this study have been previously
18 published. For details, we refer the reader to the relevant studies: Fladen and BY5 (Mort et al.,
19 2010), LF1 and LF3 (Jilbert et al., 2011), LL19 (Zillén et al., 2012) and BY15 (Jilbert and
20 Slomp, 2013b). A new ²¹⁰Pb age model was constructed for LD1. Samples from the Landsort
21 Deep (LD1) were analyzed with a Canberra BeGe gamma ray spectrometer at Utrecht
22 University. The samples were freeze-dried, homogenized, and transferred into vent-free petri
23 dishes, which were sealed in polyethylene bags and stored for 2 weeks before the
24 measurement. Each sample was measured until 200-250 ²¹⁰Pb gamma-ray counts were
25 reached. For the age determination, a constant rate of supply model (Appleby and Oldfield,
26 1983) was implemented using a background estimated from the mean counts of ²¹⁴Pb and
27 ²¹⁴Bi. For further details on the age models and the ²¹⁰Pb data for LD1, we refer to the
28 supplementary information Appendix A.

29 The age model for the site in the Fårö Deep (F80) was constructed using high resolution Mo
30 and Mn data. In 2013, an extra sediment core from this station was taken. Mini sub-cores of
31 the upper sediments, were embedded in Spurr's epoxy resin and measured by Laser Ablation -
32 Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) line scanning (see Section

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1 2.4). Due to non-linear compaction of the sediments during the embedding procedure, the
2 depth scale of the LA-ICP-MS data was adjusted by alignment to discrete sample data from
3 the corresponding core section (not shown). Subsequently, fluctuations in Mo/Al and Mn/Al
4 ratios were compared with instrumental records of bottom water oxygen conditions, and ages
5 were assigned to features in the Mo/Al and Mn/Al profiles (see Appendix A, Fig. A2). The
6 adjustment of the depth scale and the allocation of ages allowed sedimentation rates to be
7 estimated (Appendix A; Fig. A3). The 2009 multicore profiles from F80 were then tuned to
8 the dated profiles from 2013 (see Appendix A for more details).

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9 **2.4 Microanalysis**

10 Mini sub-cores of 1 cm diameter and up to ~12 cm length each were taken from the top part
11 of sediment multicores at sites LL19 and LD1 in May 2011 as described in detail by Jilbert
12 and Slomp (2013b). Briefly, the pore water was replaced by acetone and the sub-core was
13 fixed in Spurr's epoxy resin. During the whole procedure the sub-cores remained upright.
14 During the dewatering process the sediment compacted resulting in a reduction of length of
15 both sections by up to 50%. After curing, epoxy-embedded sub-cores were opened
16 perpendicular to the plane of sedimentation and the exposed internal surface was polished.

17 Line scans were performed with LA-ICP-MS, to measure high-resolution vertical profiles of
18 selected elements in the resin blocks of the two cores (Hennekam et al. 2015). A Lambda
19 Physik laser of wavelength 193 nm and pulse rate of 10 Hz was focused onto the sample
20 surface with a spot size of 120 μm . During line scanning, the sample was moved under the
21 laser beam at 0.0275 mm/s, creating an overlapping series of pulse craters. From the closed
22 sample chamber, the ablated sample was transferred to a Micromass Platform ICP-MS by He-
23 Ar carrier gas. Specific isotopes of aluminum (^{27}Al), iron (^{57}Fe), manganese (^{55}Mn), sulfur
24 (^{34}S) and molybdenum (^{98}Mo) were measured. For site LD1, bromine (^{81}Br) was also
25 measured. LA-ICP-MS data for each element were calibrated by reference to the sensitivities
26 (counts/ppm) of the glass standard NIST SRM 610 (Jochum et al., 2011) and corrected for the
27 natural abundances of the analyzed isotopes. All data are reported normalized to Al to correct
28 for variations in sample yield. For S/Al data, a further sensitivity factor was applied which
29 compensates for the contrasting relative yield of S from NIST SRM 610 with respect to
30 embedded sediments.

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1 The resin-embedded samples were also mounted inside an EDAX Orbis Micro XRF Analyzer
2 to construct elemental maps at a spatial resolution of 30 μm for manganese (Mn), calcium
3 (Ca) and sulfur (S) (Micro XRF settings: Rh tube at 30 kV, 500 μA , 300 ms dwell time, 30
4 μm capillary beam).

5 **2.5 Flux calculations**

6 The diffusive flux of manganese across the sediment-water interface (J_{sed}) was calculated
7 from the concentration gradient that was obtained from the difference in concentration in the
8 bottom water and the first porewater sample (with the depths of this first sample ranging from
9 0.25 to 2.5 cm) using Fick's first law for six sites, assuming that most dissolved Mn is in the
10 form of Mn^{2+} .

Gelöscht: To allow comparison of the data from the micro analyses with the discrete samples, the measured profiles of the LA-ICP-MS were expanded to the original length of the core section and aligned to the discrete sample data (not shown).¶

$$11 \quad J_{\text{sed}} = -\phi D_{\text{sed}} \frac{dC_{\text{Mn}^{2+}}}{dx} \quad (1)$$

12 where ϕ is the porosity (as listed in Appendix B), D_{sed} is the whole sediment diffusion
13 coefficient for dissolved Mn^{2+} , C is the dissolved Mn^{2+} concentration and x is depth in the
14 sediment. D_{sed} was calculated from the diffusion coefficient of Mn^{2+} in free solution corrected
15 for ambient salinity and temperature (D_{sw}) and porosity (Boudreau, 1997):

Gelöscht: in the pore water over the upper 0.25 to 2.5 cm of the sediment with Fick's first law for 6 sites

$$16 \quad D_{\text{sed}} = \frac{D_{\text{sw}}}{(1 - \ln \phi^2)} \quad (2)$$

17 Whenever possible (LL19, BY15 and F80), higher resolution data from the 2009 Aranda
18 cruise was used for the calculation (Table 2 and data in Appendix B).

19 **2.6 Saturation state**

20 Thermodynamic equilibrium calculations were performed for the pore water of LF3, LL19,
21 BY15, F80 and LD1 using version 3.1.1 of the computer program PHREEQC (Parkhurst and
22 Appelo, 1999) with the LLNL database. Our calculations should be seen as approximations
23 with the main purpose of providing a comparison to previous calculations by Carman and
24 Rahm (1997) and Heiser et al. (2001) to assess whether there are any indications for a change
25 in saturation state of the pore water between inflows. The LLNL database does not contain the
26 authigenic carbonate phases present in the Baltic Sea. Data from the literature (Jakobsen and
27 Postma, 1989; Sternbeck and Sohlenius, 1997; Lepland and Stevens, 1998; Huckriede and
28 Meischner 1996; Kulik et al., 2000) suggest that Baltic carbonates are predominantly Mn

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1 carbonates with a substantial contribution of Ca. Therefore, an approximation of the solubility
2 product of (Mn, Ca) CO₃ solid solutions was generated using the equations given in
3 Katsikopoulos et al. (2009). The stoichiometric solubility product (K_{st}) was calculated using
4 Mn_{0.74}Ca_{0.26}CO₃ (Kulik et al 2000) as a common ratio measured for (Mn, Ca) CO₃ solid
5 solutions in Baltic Sea sediments.

6 An equilibrium constant pK of 0.377 (Emerson et al. 1983) was used for Mn sulfide. The
7 solubility of iron sulfide from Rickard (2006) was added to the database as well as MnHS⁺ as
8 a solute (Luther et al., 1996) because it is likely abundant in pore water in sulfidic sediments
9 (Heiser et al., 2001). At sites LF3 and LD1, Fe²⁺ was below the detection limit and the
10 calculation of the saturation state with respect to FeS could not be performed. Carbonate
11 alkalinity was calculated from titration alkalinity as described by Carman and Rahm (1997).

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12 2.7 Diagenetic model for Mn

13 A simple diagenetic model for Mn was developed to assess the potential effect of changes in
14 the kinetics of reductive dissolution of Mn oxides to dissolved Mn²⁺ and subsequent Mn
15 carbonate formation in Baltic Sea surface sediments following an inflow event. Our modeling
16 is generic and addresses this research question only. Therefore, we do not attempt to describe
17 all the relevant processes potentially controlling Mn carbonate formation in the sediment nor
18 do we focus on a specific location. The model accounts for two biogeochemical processes:
19 reductive dissolution of Mn oxides to Mn²⁺ and precipitation of Mn²⁺ in the form of Mn
20 carbonates. Empirical rate laws for Mn oxide reduction and Mn carbonate formation are
21 assumed, with rates depending on first order rate constants for both processes (k_{red} and k_{prec})
22 and the sediment concentration of Mn oxide and dissolved Mn²⁺, respectively (Berner, 1980;
23 Slomp et al., 1997). The use of a first-order rate constant for a process that is more complex,
24 does not imply that all other factors are ignored. Instead, it implies that all other factors are
25 combined in the first-order rate constant (Berner, 1980). Here, the dependence of the rate of
26 Mn carbonate formation on only dissolved Mn implies that we assume that alkalinity is never
27 limiting for Mn carbonate formation. Transport is assumed to occur through diffusion (Mn²⁺)
28 and sediment burial (Mn²⁺ and both solids). Porosity (ϕ), temperature, sediment density (ρ_s)
29 and rates of sedimentation (ω) are assumed constant with depth and time. The following
30 differential equations were used:

$$1 \quad \frac{\partial C_{Mn^{2+}}}{\partial t} = D_{Mn^{2+}} \frac{\partial^2 C_{Mn^{2+}}}{\partial x^2} - \omega \frac{\partial C_{Mn^{2+}}}{\partial x} - k_{prec} C_{Mn^{2+}} + \frac{\rho_s(1-\phi)}{\phi} k_{red} C_{Mn_{oxide}} \quad (3)$$

$$2 \quad \frac{\partial C_{Mn_{oxide}}}{\partial t} = -\omega \frac{\partial C_{Mn_{oxide}}}{\partial x} - k_{red} C_{Mn_{oxide}} \quad (4)$$

$$3 \quad \frac{\partial C_{MnCO_3}}{\partial t} = -\omega \frac{\partial C_{MnCO_3}}{\partial x} + \frac{\phi}{\rho_s(1-\phi)} k_{prec} C_{Mn^{2+}} \quad (5)$$

4 where $C_{Mn^{2+}}$, $C_{Mn_{oxide}}$ and C_{MnCO_3} are the concentrations of dissolved Mn^{2+} , Mn oxides and
 5 $MnCO_3$, respectively and $D_{Mn^{2+}}$ is the diffusion coefficient of dissolved Mn^{2+} as defined in
 6 equation (2). The model code was written in R using the marelac (Soetaert et al., 2010) and
 7 ReacTran (Soetaert and Meysman, 2012) packages. The model domain is represented by a
 8 one-dimensional grid of 1000 cells that captures the interval from the sediment-water
 9 interface to a depth of 1 cm. Environmental parameters typical for surface sediments in the
 10 deep basins of the Baltic Sea and boundary conditions were assumed as defined in Table 3.

11 Here, we assess a scenario for Baltic Sea sediments where Mn oxides are deposited during a
 12 period of oxic bottom water conditions for 4 months directly after a North Sea inflow
 13 followed by a period of two months in which no Mn oxides are deposited because of the
 14 return of bottom water anoxia (Table 3; Section 4.1). We assume that there is no Mn in the
 15 sediment (in any form) at the start of the scenario, consistent with Mn being low or
 16 absent in surface sediments in the Gotland basin between inflows (Figure 4). We set k_{prec}
 17 to $5,000 \text{ yr}^{-1}$, placing the maximum rate of Mn carbonate formation in the model calculations
 18 in the upper range given by Wang and Van Cappellen (1996). We then assess the response of
 19 benthic fluxes of Mn^{2+} , rates of formation of Mn carbonate in the sediment and profiles of the
 20 various Mn forms to variations in k_{red} when assuming values of either 0.1, 1, 10, 100 or 1000
 21 yr^{-1} during 4 months of the simulation followed by a period of two months with a k_{red} of 1000
 22 yr^{-1} (i.e. representing rapid Mn oxide reduction after the return of anoxic conditions). By
 23 varying k_{red} , we wish to capture a wide range in the availability of reductants for Mn oxides in
 24 the surface sediment. Values of k_{red} estimated for different sedimentary environments overlain
 25 by oxic bottom waters in the North Sea range from $0.04 - 150 \text{ yr}^{-1}$ (Slomp et al., 1997). The
 26 slightly wider range assumed here is reasonable because of the more important role of
 27 anaerobic pathways of organic matter degradation in deep basin sediments of the Baltic Sea
 28 compared to those in the North Sea (e.g. Mort et al., 2010 versus Slomp et al., 1997). To

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1 assess the robustness of our results, we also perform the same simulations with even higher
2 k_{prec} values (up to 30,000 yr⁻¹).

3 **3 Results**

4 At the time of sampling, bottom waters were oxic at the Fladen and LF1 sites in the eastern
5 Gotland Basin, hypoxic at the Bornholm Basin site BY5, and anoxic and sulfidic at all other
6 locations (Table 1). Pore water Mn concentrations increase with depth in the sediment at most
7 sites (Figure 2; Appendix B). At the Fladen site, however, pore water Mn concentrations
8 decrease again below ca. 5 cm and at the eastern Gotland Basin sites LF1 and LF3, Mn
9 concentrations are lower than at other sites. Pore water Fe shows a subsurface maximum at
10 the Fladen and LF1 sites, but is low or absent at all other sites. Pore water Ca²⁺ concentrations
11 show little change with depth and are consistent with the salinity gradient in the Baltic Sea.
12 Alkalinity and ammonium concentrations increase with sediment depth simultaneously with a
13 decline in sulfate. CH₄ is present at depth where sulfate is depleted at the sites in the Fårö
14 Deep (F80) and Landsort Deep (LD1) (Appendix B). Similar to Ca²⁺, sulfate concentrations in
15 the bottom water at the different stations are consistent with the salinity gradient in the Baltic
16 Sea (Table 1). Concentrations of hydrogen sulfide in the pore water > 2 mM are found at the
17 Fårö Deep and Landsort Deep sites F80 and LD1. The pore waters are supersaturated with
18 respect to Mn carbonate below the surface sediment at the Landsort Deep. With the exception
19 of LF3, the other hypoxic and anoxic sites reach saturation only at greater depth. For Mn
20 sulfide, in contrast, supersaturation is only observed at the Landsort Deep site, LD1 (Figure 3)
21 and below 35 cm at site F80. Pore waters were supersaturated with respect to FeS at the sites
22 in the Northern Gotland Basin (LL19), in the Gotland Deep (BY15) and Fårö Deep (F80)
23 (Appendix B). We note that degassing of CO₂ during centrifugation may have led to a shift in
24 pH to higher values, thereby enhancing the degree of saturation with respect to carbonate and
25 sulfide minerals. Nevertheless, an upward shift of ca. 0.5 pH units due to this effect would not
26 greatly affect the observed trends with depth and contrasts between stations in the calculated
27 saturation states presented. Calculated diffusive fluxes of dissolved Mn vary from 81 to 236
28 $\mu\text{mol m}^{-2} \text{d}^{-1}$, with the highest efflux from the sediment being observed at the hypoxic
29 Bornholm Basin site BY5 and in the anoxic Landsort Deep (LD1)(Table 2).

30 Average sedimentation rates vary significantly between sites, with 3- to 4-fold higher rates at
31 Fladen and in the Landsort Deep (LD1) when compared to the oxic site in the eastern Gotland
32 Basin (LF1) and Bornholm Basin (BY5)(Table 1; Figure 4). Sediments are highly porous.

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1 | with porosities in the surface sediment ranging from 87 to 99 vol% (Appendix B) and rich in
2 | organic carbon (TOC) with maxima of ca. 5 wt% at the oxic sites Fladen and LF1 and ca. 16
3 | wt% at the anoxic sites (Figure 4). Whereas changes in TOC with depth at Fladen and LF1 are
4 | relatively small, distinct enrichments in TOC are observed in the upper part of the sediment at
5 | all anoxic sites. High contents of total Al, which is a proxy for clays, are consistent with the
6 | presence of fine-grained sediments throughout the cores (Appendix B). Total sulfur contents
7 | are low at Fladen, but are higher at all other sites, and show considerable variation with depth
8 | in the sediment. Mn is enriched in the surface sediment at Fladen, but is nearly absent at the
9 | LF1, BY5 and LF3 sites. At sites LL19, BY15 and F80, Mn is present but mostly observed at
10 | greater depth in the sediment. The upper 30 cm of the sediment at site LD1 is highly enriched
11 | in Mn. Sediment Ca is high at Fladen, is enriched in the surface sediment at site LF1, is low at
12 | sites BY5, LF3 and LL19 and follows the pattern in Mn at sites BY15, F80 and LD1.
13 | Sediment Fe typically ranges from 2 to 6 wt% and there is a trend towards lower Fe contents
14 | in the upper 5 to 20 cm of the sediment, following an initial maximum at the bottom of the
15 | TOC-rich interval at many sites (Appendix B). This upward declining trend is even more
16 | apparent when the Fe contents are normalized to Al (Figure 4). Sediment Mo is low at the
17 | Fladen, LF1, BY5 and LF3 sites but is enriched at the other sites, where profiles largely
18 | follow those of TOC (Figure 4).

19 | The LA-ICP-MS line-scans of resin-embedded surface sediments at site LL19 in the Northern
20 | Gotland Basin (Figure 5A) support the results of the discrete sample analysis (Figure 4) and
21 | confirm that there are very few Mn rich laminae in recent sediments at this location. Whereas
22 | most of the minor enrichments of Mn are correlated with Fe, S and Mo (Figure 5A), three
23 | peaks (at 3.6, 3.9 and 4.6 cm) are independent of these elements, suggesting that these Mn
24 | enrichments dominantly consist of carbonates. This is confirmed by the Micro-XRF maps
25 | (Figure 5B) of the corresponding interval, which indicate coincident Mn and Ca-rich layers.
26 | The maps show clear Mn carbonate layers at ~3.9 cm and ~4.6 cm. A third enrichment at 3.6
27 | cm is less continuous and is only represented by one spot in the map. The two distinct Mn
28 | carbonate layers can be linked to inflow events in 1993 and 1997, using the ²¹⁰Pb-based age
29 | model for this site, after correction for compaction of the sediment during embedding.

30 | In the surface sediments of the Landsort Deep site (LD1), in contrast, a large number of Mn
31 | enrichments with much higher concentrations than at LL19 are observed (Figure 4 and 5).
32 | The LA-ICP-MS line scans show that the highest values often coincide with enrichments in S,

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1 Mo and Br but are not related to maxima in Fe. The micro-XRF-maps of Mn, Ca and S
2 confirm that enrichments in Mn are present as discrete layers. The RGB (Mn, Ca, S)
3 composite reveals two different compositions for the Mn enrichments. The purple layers in
4 the RGB composite are a result of enrichments of Mn (red) and S (blue) in the same pixel,
5 suggesting the presence of Mn sulfide. Other layers and spots are orange to yellow, indicating
6 coincident enrichments of Ca (green) and Mn, suggesting carbonate enrichments (Figure 5B).

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7 The change in the integrated amount of Mn oxide and Mn carbonate in the sediment with time
8 as calculated with the diagenetic model, depends on the value of the rate constant for the
9 reduction of Mn oxides (k_{red}) assumed for the period with oxic (4 months) bottom waters
10 (Figure 6A and B). The amount of Mn oxide that is preserved during this phase decreases
11 with increasing values of k_{red} . When k_{red} is low, most of the Mn oxide deposited on the
12 sediment is preserved during the first 4 months of the simulation. The results show that the
13 more Mn oxide is preserved during the oxic phase, the more Mn carbonate forms during the
14 following anoxic phase, because less dissolved Mn escapes to the overlying water through
15 diffusion. In runs with low values of k_{red} , Mn carbonate is mostly formed in the 2-month
16 anoxic phase. At intermediate values of k_{red} , there is also formation of Mn carbonate in the
17 oxic phase. At high values of k_{red} , Mn carbonate formation is negligible. Corresponding
18 changes in integrated amounts of dissolved Mn in the sediment and benthic fluxes of Mn
19 during the simulations are shown in Appendix C.

Gelöscht: Benthic fluxes of Mn^{2+} and rates of Mn carbonate formation

Gelöscht: While benthic fluxes of Mn^{2+} increase with increasing values of k_{red} , especially during the first 4 months of the simulation, rates of Mn carbonate formation integrated with depth decrease (Figure 6).

20 Examples of depth profiles of Mn oxides, dissolved Mn and Mn carbonate at various key
21 stages of the simulation illustrate the dependence of Mn carbonate formation on the rate of
22 reduction of Mn oxides during the oxic phase (Figure 6C). After 4 months, a large amount of
23 Mn oxides has accumulated in the surface sediment when k_{red} is equal to 0.1 yr^{-1} . Such an
24 enrichment is absent when k_{red} is 1000 yr^{-1} . High dissolved Mn concentrations at the onset of
25 the anoxic phase (shown for 4 months and 8 hours) and the formation of a Mn carbonate-rich
26 layer (shown for the end of the simulation) is restricted to the scenario which allows the Mn
27 oxides to accumulate. Runs with a higher rate constant for precipitation of Mn carbonates
28 (k_{prec}) lead to more sharply defined peaks in Mn carbonate and more Mn carbonate formation
29 at higher k_{red} values, but the same trends in fluxes and rates with varying k_{red} are observed
30 (not shown).

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Gelöscht: at the end of the 4 month oxic phase and of Mn carbonates at the end of both the oxic and anoxic phases at 6 months illustrate the dependence of Mn carbonate formation in the model on the rate of reduction of Mn oxides. Example profiles of Mn^{2+} at the start of the anoxic phase are also shown.

1 4 Discussion

2 4.1 Sediment Mn cycling in the Baltic Sea

3 Our results indicate major differences in Mn dynamics in the varied depositional settings of
4 the Baltic Sea. Although located in the Kattegat far from the euxinic basins, processes at the
5 Fladen site (Figure 2 and 3) can be used to illustrate the typical processes at oxic sites. Here,
6 Mn cycling is largely internal to the sediment and the Mn that is released to the pore water at
7 depth mostly reprecipitates upon upward diffusion into the oxic surface sediment. At the
8 hypoxic site in the Bornholm Basin (BY5) there is no clear sediment Mn enrichment but there
9 is release of dissolved Mn to the pore water, presumably due to dissolution of Mn oxides,
10 within the upper 15 cm of the sediment. At this site, the highest diffusive Mn flux from the
11 sediment to the water column was found (Table 2). At one of the sites on the slope of the
12 eastern Gotland Basin (LF1), there is a significant release of dissolved Mn to the overlying
13 water but the sediments at this site are low in solid-phase Mn. This suggests that the source of
14 Mn at this site may be of a transient nature. Our results highlight that sediments in hypoxic
15 areas may act as sources of Mn to the water column, with subsequent lateral transfer
16 potentially bringing this Mn to the deep basins (Huckriede and Meischner, 1996; Jilbert and
17 Slomp, 2013a; Lyons and Severmann, 2006; Scholz et al., 2013).

18 The pore water profiles of the 4 anoxic sites in the various deep basins (LL19, BY15, F80,
19 and LD1) all are indicative of release of Mn to the pore water, either from reductive
20 dissolution of Mn oxides or dissolution of Mn carbonates due to undersaturation (e.g. Heiser
21 et al., 2001; Jilbert and Slomp, 2013a). As a result, diffusive Mn fluxes from the sediment to
22 the water column are also observed at all these deep basin sites where it remains trapped
23 below the redoxcline in the water column. Although reoxidation of the Mn and formation of
24 mixed phases of Mn oxides and Fe-(III)-associated phosphates upon upward diffusion of Mn
25 into the redoxcline occurs (Dellwig et al., 2010; Turnewitsch and Pohl, 2010), sinking of
26 these phases into sulfidic waters leads to subsequent reductive redissolution.

27 Due to the seasonal and inflow-related changes in redox conditions in the Baltic Sea, the lack
28 of detailed data sets on dissolved Mn concentrations in the water column, and our very limited
29 number of study sites, we cannot accurately estimate the different reservoirs of Mn and the
30 importance of the present-day source of Mn from sediments overlain by oxic and hypoxic and
31 anoxic bottom waters at the basin scale. Nevertheless, we will attempt to make a rough

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1 | quantification using the data that are available and will then compare this to estimates from
2 | the literature.

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3 | Taking an average deep water volume of 2,000 km³, average hypoxic area of 47,000 km²
4 | (Carstensen et al., 2014), and a deep water concentration of Mn of 8 μM (Löffler et al. 1997
5 | as cited by Heiser et al., 2001), the amount of Mn in the deep water is estimated at 1.6 x 10¹⁰
6 | mol or 0.33 mol m⁻². The range of Mn fluxes estimated in this study (0 to 236 μmol m⁻² d⁻¹;
7 | Table 2) is comparable to benthic fluxes measured with in-situ chambers in other areas of the
8 | Baltic Sea (e.g. the Gulf of Finland; Pakhomova et al., 2007) as well as those estimated from
9 | pore water profiles acquired in the 1990's (e.g. Heiser et al., 2001). If we assume that a flux
10 | of ca. 90 μmol m⁻² d⁻¹ is representative for the sediments overlain by hypoxic and anoxic
11 | bottom waters (Table 2; based on the fluxes for LL19, F80 and BY15), we calculate a yearly
12 | flux of 0.033 mol m⁻² from those sediments, which is equivalent to 10% of the inventory in
13 | the water column. In similar calculations, Heiser et al. (2001) estimated the amount of Mn in
14 | the Gotland Deep to be equal to 0.8 mol m⁻². With our estimate of the benthic flux, this would
15 | lead to a contribution of the annual benthic flux of less than 5%. We note, however, that the
16 | role of the benthic flux of Mn from hypoxic sediments will vary spatially and may be biased
17 | towards high values because of preferential sampling of sites with a relatively high sediment
18 | accumulation rate in most pore water studies. This may explain the one order of magnitude
19 | lower benthic fluxes of Mn reported for the Gotland Deep area in 1999-2001 of ca. 7-8 μmol
20 | m⁻² d⁻¹ by Neretin et al. (2003) when compared to those in our study (Table 2).

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21 | Benthic fluxes of Mn are also expected to be high upon the reestablishment of bottom water
22 | anoxia after an inflow and then decline with time (Neretin et al., 2003). The exact impact of
23 | inflows on the oxygenation of the bottom waters in the deep basins of the Baltic Sea varies
24 | from site to site, as it depends on the volume and oxygen content of the inflowing water, its
25 | pathway and the oxygen concentration in the receiving basin (e.g. Carstensen et al., 2014),
26 | with the general flow of water in the deep basins going from the Gotland to the Fårö and the
27 | Landsort Deep (Holtermann et al., 2012). For example, the bottom water in the Gotland Deep
28 | was free of hydrogen sulfide for 4 months following the inflow of 1993-1994 (Neretin et al.,
29 | 2003; Yakushev et al., 2011) whereas the Landsort Deep was less affected because the bottom
30 | water at the time already contained oxygen (Figure 7). Using biogeochemical modeling of a
31 | typical inflow in the Gotland Deep area, Yakushev et al. (2011) showed that dissolved Mn in
32 | the water column was oxidized to Mn oxides and settled to the bottom over a time period of

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1 months. Dissolved Mn appeared in the water column again upon the return of bottom water
2 anoxia and steady state conditions in the water column were established in the model after ca.
3 1.5 years.

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4 In their study, Yakushev et al. (2011) concluded that sediments play only a minor role as a
5 source of Mn a few years after an inflow. Likely, the large pool of Mn in the water column of
6 the deep basins was mostly released from the formerly oxic sediments during the initial
7 expansion of hypoxia during the 20th century. Based on the fact that, apart from the changes in
8 Mn inventory between inflows, there is no clear trend in water column Mn concentrations in
9 the Baltic Sea with time over recent decades (Pohl and Hennings, 2005), and our observation
10 that the burial of Mn has decreased at most sites (Figure 4), it is likely that the present-day
11 Mn shuttling from the oxic and hypoxic areas around the deep basins is not as important
12 quantitatively as a source of Mn to the deep basins as it was at the onset of hypoxia early in
13 the 20th century.

14 Notably, Yakushev et al. (2011) consider Mn(III) besides Mn(II) in their model for
15 biogeochemical dynamics in the water column in the Gotland Deep. Dellwig et al. (2012)
16 found recently that Mn(III) is an important component in the water column Mn cycle in the
17 Landsort Deep but not in the Gotland Deep. Further work is required to elucidate the potential
18 importance of this finding to Mn dynamics in the Baltic Sea, its impact on other
19 biogeochemical cycles (e.g. Pakhomova and Yakushev, 2013), its role in the sediments, and
20 impacts on Mn sequestration (e.g. Madison et al., 2011). Field studies of Mn dynamics in the
21 water column and sediment during and directly after an inflow would be of particular value.

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22 4.2 Manganese sequestration in the anoxic basins

23 Formation of Mn bearing carbonates in the Gotland Basin and Landsort Deep is generally
24 described as being ubiquitous after inflows (e.g. Jakobsen and Postma, 1989). We observe
25 such Mn carbonate enrichments in all our deep basin cores, with the magnitude of the
26 enrichment increasing with water depth (Figure 4). We suggest that this water depth effect
27 between the deep basin sites is due to increased focusing of particulate Mn oxides precipitated
28 during inflow events with water depth, combined with a high alkalinity in the deep basins
29 linked to organic matter degradation by sulfate reduction. Increased focusing of Mn oxides
30 with water depth has been observed in other marine systems (e.g. Slomp et al., 1997) and high

Gelöscht: Between inflows, when bottom waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are typically assumed to be undersaturated with respect to Mn carbonates down to a depth of ~5 to 8 cm based on saturation state calculations for idealized minerals (Figure 3)(Carman and Rahm, 1997; Heiser et al., 2001). The dissolution of Mn oxides in the surface sediment following an inflow of oxygenated North Sea water is thought to lead to high Mn²⁺ concentrations in the pore water and strong oversaturation with respect to Mn carbonates, although this has not been proven (Huckriede and Meischner, 1996; Sternbeck and Sohlenius, 1997; Heiser et al., 2001). Various authors have correlated such inflow events to specific accumulations of Mn carbonate in sediments of the Gotland Basin (e.g. Heiser et al., 2001; Neumann et al., 1997).

1 alkalinity in sulfate-bearing organic rich sediments overlain by an anoxic water column are
2 typically linked to organic matter degradation through sulfate reduction (Berner et al., 1970).

3 Our microanalysis results show that the Mn carbonate enrichments at site LL19 are highly
4 laminar in character, implying rapid precipitation at or near the sediment-water interface.
5 Furthermore, these Mn carbonate enrichments occur independently of enrichments in Mo and
6 S. Sedimentary Mo can be used as a proxy for sulfidic conditions close to the sediment-water
7 interface, due to the conversion of seawater oxymolybdate to particle-reactive thiomolybdate
8 in the presence of hydrogen sulfide (Erickson and Helz, 2000). Although the ultimate burial
9 phase of Mo in sulfidic sediments is still debated (e.g., Helz et al., 2011), Mo concentrations
10 have successfully been used to reconstruct the redox history of the bottom water in restricted
11 coastal basins (Adelson et al., 2001; Jilbert and Slomp, 2013a). Sulfur enrichments in
12 sediments are typically associated with Fe-sulfides. These can form as the result of reduction
13 of Fe(III) oxides with sulfide or organic matter (Boesen and Postma, 1988), and thus Fe
14 sulphides can also be indicative of sulfidic conditions close to the sediment-water interface.

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15 The independence of these Mn enrichments from those of Mo and S suggests relatively oxic
16 conditions at the time of Mn deposition. Both lines of evidence support the interpretation of
17 Mn carbonate precipitation following inflow events (Sternbeck and Sohlenius, 1997). Our age
18 model suggests that the two pronounced Mn carbonate layers at the base of the surface-
19 sediment resin-embedded block (Figure 5) correspond to inflows in 1993 and 1997 (Matthäus
20 and Schinke, 1999).

Gelöscht: carbonate precipitation

21 Mn enrichments at the Landsort Deep site LD1 occur more frequently when compared to
22 other deep basin sites (Figure 4), as observed in earlier work (Lepland and Stevens, 1998). In
23 the Landsort Deep, Lepland and Stevens (1998) attributed the enrichments to the relatively
24 high alkalinity. Our pore water results show that alkalinity is similar to that in the Fårö Deep
25 (F80), but the pore water Mn concentrations at the Landsort Deep site are much higher than
26 elsewhere (>1 mM versus <0.26 mM of Mn). This may be related to the fact that the Landsort
27 Deep is the deepest basin in the Baltic Sea and its geometry makes it an excellent sediment
28 trap. Indeed, sediment deposition rates at the Landsort Deep are much higher than in the other
29 Deeps (Lepland and Stevens, 1998; Mort et al., 2010), perhaps as much as 6 times higher,
30 (Expedition 347 Scientists, 2014). Sediment focusing is also expected to lead to a higher input
31 of organic matter and Mn oxides to this basin. Given that rates of mineral dissolution are
32 expected to depend on the amount of material present, corresponding rates of input and

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1 dissolution of Mn oxide minerals in the sediment are likely higher in the Landsort Deep than
2 at other sites. Thus, we suggest that differences in focusing of the sediment may explain the
3 observed differences in pore water chemistry and Mn sequestration. The differences in pore
4 water chemistry will also likely impact the exact solid phases formed in the sediments of the
5 various deep basins.

6 The high-resolution analyses for the Landsort Deep site (LD1) also show that, besides Mn
7 carbonate enrichments, there are several distinct layers of Mn sulfide in the surface sediments
8 (Figure 5). These appear to coincide with enrichments in Mo, suggesting formation of Mn
9 sulfides during intervals of more reducing conditions (Mort et al., 2010). Furthermore, we
10 observe simultaneous enrichments of Br (Figure 5), which suggests higher organic carbon
11 contents (Ziegler et al., 2008). These results could imply that increased rates of sulfate
12 reduction linked to elevated inputs of organic material to the sediments drive the formation of
13 Mn sulfide by contributing to an excess of sulfide over Fe. We note that the interval presented
14 in the XRF map covers only a few years of sediment accumulation, possibly suggesting rapid
15 changes in Mn mineralogy in response to seasonal variability of the organic matter flux
16 (Figure 5). Primary productivity in the Baltic Sea is known to vary seasonally (Bianchi et al.,
17 2002; Fennel, 1995). Further work is required to determine conclusively the mechanisms of
18 MnS formation. While the presence of MnS has been shown for the earlier anoxic time
19 intervals in the Baltic (Böttcher and Huckriede, 1997; Lepland and Stevens, 1998), this is the
20 first time Mn sulfides are reported for such near-surface sediments in the Baltic Sea.

21 The contrasting controls on Mn mineral formation in the Landsort Deep, compared to the
22 other deep basin sites, are further illustrated by a comparison of the trends. This supports our
23 hypothesis that in total Mn and Mo concentrations (Figure 4) with measured bottom water
24 oxygen concentrations for the period 1955 to 2010 (ICES Dataset on Ocean Hydrography
25 2014) for sites in the northern Gotland Basin (LL19) and the Landsort Deep (LD1) (Figure 7).
26 At site LL19, Mn enrichments in the sediments coincide with low values of Mo in the
27 sediment and inflows of oxygenated water. This suggests that Mn burial is enhanced under
28 more oxygenated bottom water conditions. At LD1, in contrast, high Mn contents are
29 observed from 1965 onwards, independent of inflows, with the highest Mn values coinciding
30 with periods with the highest sulfide concentrations that occur in particular since the year
31 2000. This supports our hypothesis that the formation of Mn carbonate minerals in the
32 Landsort Deep is not always related to inflows and that the Mn oxide supply is higher and

1 | more continuous when compared to the other basins, due to the much stronger sediment
2 | focusing related to the peculiar basin geometry.

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3 | 4.3 Changes in Mn burial linked to expanding hypoxia

4 | Strikingly, the more reducing conditions in the Gotland Basin (LL19, BY15) and Fårö Deep
5 | sites (F80) over the past decades, as recorded in the Mo profiles (Figures 4 and 7), are
6 | accompanied by a strong reduction in sediment Mn burial. Given the suggested link between
7 | Mn burial and inflows, it is important to assess the occurrence of these inflows. During the
8 | past two decades, there were two major (1993, 2003) and several minor inflow events (e.g.
9 | 1997) into the Baltic Sea. The event in 1993 was one of the strongest in the last 60 years
10 | (Matthäus et al., 2008) and the inflow of 2003 (Feistel et al., 2003) was weaker but still
11 | significant enough to reoxygenate the bottom water of the deep basins (Figure 7).

12 | Nevertheless, at LL19, Mn sequestration in the sediment between 2000 and 2010 has been
13 | negligible and the inflow in 2003 is not recorded as a Mn carbonate enrichment (Figure 7),
14 | whereas, in the high resolution geochemical analyses, Mn layers are clearly visible in both the
15 | LA-ICP-MS and micro-XRF scans (Figure 5) and can be linked to the inflows of 1993 and
16 | 1997. A similar “missing” Mn carbonate layer was observed by Heiser et al. (2001) in the
17 | Gotland Deep and attributed to re-dissolution of Mn carbonate linked to resuspension events
18 | and mixing of the sediment into unsaturated bottom waters, but our cores were clearly
19 | laminated and the ²¹⁰Pb profiles also show no evidence for mixing. We therefore conclude
20 | that, with the increased hypoxia and euxinia in the Baltic Sea, Mn oxides are no longer
21 | converted to stable Mn carbonates following inflows.

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22 | The formation of Mn carbonates in Baltic Sea sediments is typically believed to be induced
23 | by the high alkalinity linked to organic matter degradation combined with high dissolved Mn,
24 | concentrations in the surface sediment. These high dissolved Mn concentrations are thought
25 | to be the result of reductive dissolution of Mn oxides that have formed at the sediment-water
26 | interface directly following an inflow of oxygenated North Sea water. When hypoxia is re-
27 | established and the oxides are dissolved (Lepland and Stevens, 1998), supersaturation with
28 | respect to Mn carbonates is assumed to be reached in the surface sediment and not only at
29 | depths below ca. 5-10 cm (Figure 3). What can inhibit the formation of these Mn carbonates?
30 | One possibility is that at high pore water sulfide concentrations, Mn sulfides form instead of
31 | Mn carbonates, but given that there is negligible Mn enrichment in the upper sediments of
32 | F80, BY15 and LL19 today, we can exclude that possibility. Mn carbonate formation could

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1 be reduced if alkalinity declined, but alkalinity in the bottom waters of the Gotland Deep has
2 in fact increased recently (e.g. Ulfssbo et al., 2011), possibly due to higher rates of anaerobic
3 mineralization linked to eutrophication (Gustafsson et al., 2014). High phosphate
4 concentrations in the surface sediment may potentially negatively affect the rate of Mn
5 carbonate formation (Mucci, 2004), but there is no evidence for a significant rise in dissolved
6 phosphate in the pore water of Gotland Basin sediments over the past decades (e.g. Carman
7 and Rahm, 1997; Hille et al., 2005; Jilbert et al., 2011). Alternatively, we hypothesize that the
8 Mn oxides that are formed following modern inflow events might be reductively dissolved
9 faster than previously. As a consequence, the dissolved Mn, released from the oxides could
10 then escape to the overlying water instead of being precipitated in the form of Mn carbonate.
11 This hypothesis is consistent with the results of the simple diagenetic model where high rates
12 of Mn oxide reduction lead to less Mn carbonate formation (Figure 6).

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13 There are multiple possible reductants for Mn oxides in marine sediments, including sulfide,
14 Fe(II) (e.g. Canfield and Thamdrup, 2009), NH₄⁺ (e.g. Luther et al., 1997), and CH₄ (Beal et
15 al., 2009), with the role of the latter two reductants in marine sediments still being debated.
16 Given that the dissolved Fe and CH₄ concentrations in the pore waters of the surface
17 sediments of the Gotland Basin area are negligible, these constituents are unlikely to play an
18 important role as a reductant for Mn oxides in the northern Gotland Basin (LL19), Fårö Deep
19 (F80) and Gotland Deep (BY15) sites. Furthermore, there is no evidence for a major recent
20 change in pore water CH₄ concentrations in the surface sediments. There is evidence,
21 however, for a recent rise in the bottom water sulfide concentrations in the deep basins of the
22 Baltic Sea (Figure 7) linked to eutrophication (Carstensen et al., 2014). As shown for the
23 northern Gotland Basin site (LL19), the more persistent presence of high concentrations of
24 bottom water sulfide and enrichments in sediment Mo, coincide with the decline in Mn in the
25 sediment (Figure 7).

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26 We hypothesize that Mn oxides that are formed following modern inflow events and that are
27 deposited on the seafloor (Heiser et al., 2001) are no longer being converted to Mn carbonates
28 because of higher pore water sulfide concentrations and the rapid onset of sulfidic conditions
29 in the overlying waters. These higher sulfide concentrations are likely the direct result of
30 increased sulfate reduction driven by the ongoing rise in productivity in the Baltic Sea
31 (Gustafsson et al., 2012, 2014; Carstensen et al, 2014). The observed decline in Fe/Al at our
32 deep basin sites (Figure 3) suggests more muted shuttling of Fe oxides from shelves to the

Gelöscht: ambient concentrations of sulfide in the bottom water and in the pore water

1 deeps linked to the expanding hypoxia (e.g. Scholz et al., 2014) which may have reduced the
2 buffer capacity of the sediments for sulfide (e.g. Diaz and Rosenberg, 2008).

3 The rate of reduction of Mn oxides with sulfides is assumed to linearly depend on the
4 concentration of sulfide according to the following rate law (Wang and Van Cappellen, 1996):

$$5 \quad R = k C_{TS} C_{Mn\text{oxides}} \quad (6)$$

6 where k is a rate constant (with a value $<10^8 \text{ yr}^{-1}$) and C_{TS} stands for the total sulfide
7 concentration, i.e. the sum of the concentrations of H_2S and HS^- (in M). In our modeling
8 approach, the rate law for this process is assumed equal to

$$9 \quad R = k_{\text{red}} C_{Mn\text{oxides}} \quad (7)$$

10 Thus, if sulfide is the reductant, k_{red} can be assumed to be equivalent to the product of k and
11 C_{TS} . Sulfide will be absent in oxygenated pore waters, i.e. can be below $1 \mu\text{M}$ in the surface
12 sediment, but also can range up to 1.1 to 2.2 mM as observed at sites F80 and LD1 (Figure 2;
13 Appendix B). Corresponding k_{red} values for surface sediments in the Baltic Sea would then be
14 expected to range over 3-4 orders of magnitude and stay below 10^5 yr^{-1} , which **is consistent**,
15 with our assumptions. Mn carbonate formation is found to critically depend on the value of
16 k_{red} (Figure 6). **Although** we are aware that factors **other** than the availability of Mn are also
17 critical to Mn carbonate formation, these model results support our suggestion that a recent
18 rise in the pore water and bottom water **sulfide concentrations** may have made the surface
19 sediments more hostile to the preservation of Mn oxide after an inflow and might contribute
20 to their reduction. **Consequently, more dissolved Mn** could then escape to the overlying water
21 instead of being precipitated in the form of Mn carbonate, explaining the lack of recent Mn
22 enrichments.

23 **4.4 Implications for Mn as a redox proxy**

24 In the classic model of Calvert and Pedersen (1993), Mn enrichments in sediments are
25 indicative of either permanent or temporary oxygenation of bottom waters. Sediments of
26 permanently anoxic basins, in contrast, are assumed to have no authigenic Mn enrichments
27 because there is no effective mechanism to concentrate Mn oxides. Our results for the
28 Gotland Deep area indicate that the temporary oxygenation of the basin linked to inflows is
29 no longer recorded as a Mn enrichment in the recent sediment when hypoxia becomes basin-
30 wide. Thus, a decline in Mn burial (or a complete lack of Mn) in geological deposits in

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1 combination with indicators for water column euxinia, such as elevated Mo contents, may
2 point towards expanding hypoxia, but does not exclude temporary oxygenation events.
3 Strikingly, only very little Mn was buried at sites F80 and LL19 during the previous period of
4 hypoxia in the Baltic Sea during the Medieval Climate Anomaly (Jilbert and Slomp, 2013b)
5 as well as at the end of the Holocene Thermal Maximum at site LL19 (Lenz et al., 2014). It is
6 believed that hypoxia was equally intense and widespread in the basin at the time as it is
7 today. Our results for the Landsort Deep suggests that Mn enrichments may also form
8 frequently in an anoxic basin as Mn carbonates and sulfides if the input of Mn from the
9 surrounding area is exceptionally high due to sediment focusing. Mn enrichments in
10 geological deposits thus can be indicative of both oxic and anoxic depositional environments,
11 emphasizing the need for multiple redox proxies.

12 5 Conclusions

13 We show that the most recent sediments in the Fårö Deep and Gotland Deep contain low
14 concentrations of Mn near the sediment surface. We hypothesize that this is due to the
15 expansion of the area with hypoxic bottom waters and the development of more continuous
16 bottom water euxinia over the past decades, linked to ongoing eutrophication and possibly
17 due to the reduced input of Fe-oxides that can act as a sink for sulfide. The high ambient
18 sulfide concentrations in the sediment and water column after an inflow event are thought to
19 be more conducive to faster dissolution of Mn oxides, leading to more loss of dissolved Mn to
20 the water column and less formation of Mn carbonate. Our hypothesis is supported by the
21 results of a simple diagenetic model for Mn. It is also consistent with the general
22 interpretation of sediment records of Mn in paleoceanography and the use of Mn as a redox
23 proxy where the absence of Mn carbonates in sediments is assumed to be indicative of euxinic
24 bottom waters (e.g. Calvert and Pedersen, 1993). In the Landsort Deep, in contrast, Mn
25 sulfides and carbonates are still being precipitated. This could be due to strong focusing of
26 Mn rich sediment particles and high rates of sediment accumulation in the Landsort Deep.
27 Our results indicate that sediment Mn carbonates in the other deep basins of the Baltic Sea no
28 longer reliably and consistently record inflows of oxygenated North Sea water. This has
29 implications for the use of Mn enrichments as a redox proxy when analyzing geological
30 deposits.

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10

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- 12
- 13

1 Table 1. Characteristics of the 8 study sites in the Baltic Sea. Redox: bottom water redox
 2 conditions at the time of sampling. Pore water samples were obtained during every cruise and
 3 were similar between years at each station. Here, the most complete data sets for each station
 4 are presented. Average sedimentation rates for the last 30 years are based on ²¹⁰Pb dating.

| Site name | Location | Cruise | Position | Water depth (m) | Sedimentation Rate (cm yr ⁻¹) | Redox | Salinity |
|-----------|------------------------|---|------------------------|-----------------|---|------------------------------|----------|
| Fladen | Fladen | R/V Skagerak Sept. 2007 | 57°11.57N 11°39.25E | 82 | 1.0 | oxic | 34.2 |
| LF1 | Northern Gotland Basin | R/V Aranda May/June 2009 | 57°58.95N 21°16.84E | 67 | 0.25 | oxic | 8.2 |
| BY5 | Bornholm Basin | R/V Skagerak Sept. 2007 | 55°15.16N 15°59.16E | 89 | 0.23 | O ₂ =4.0 μM | 16.2 |
| LF3 | Eastern Gotland Basin | Sediment: R/V Aranda May/June 2009 Pore water: R/V Pelagia May 2011 | 57°59.50N 20°46.00E | 95 | 0.50 | H ₂ S=2.9 μM | 10.1 |
| LL19 | Northern Gotland Basin | Sediment: R/V Aranda May/June 2009 Pore water: R/V Heincke July 2010 | 58°52.84N 20°18.65E | 169 | 0.30 | H ₂ S=19. 9 μM | 11.4 |
| BY15 | Gotland Deep | Sediment R/V Aranda May/June 2009 Pore water: | 57°19.20N 20°03.00E | 238 | 0.27 | H ₂ S=74. 1 μM | 12.5 |

| | | | | | | | |
|-----|---------------|-------------|-----------|-----|------|----------------------|------|
| | | R/V Heincke | | | | | |
| | | July 2010 | | | | | |
| F80 | Fårö Deep | Sediment: | 58°00.00N | 191 | 0.55 | H ₂ S=45. | 12.0 |
| | | R/V Aranda | 19°53.81E | | | 6 µM | |
| | | May/June | | | | | |
| | | 2009 | | | | | |
| | | Pore water: | | | | | |
| | | R/V Heincke | | | | | |
| | | July 2010 | | | | | |
| LD1 | Landsort Deep | R/V Pelagia | 58°37.47N | 416 | 0.77 | anoxic | 10.6 |
| | | May 2011 | 18°15.23E | | | and sulfidic | |

1

1 Table 2. Diffusive fluxes of Mn across the sediment-water interface at all 6 sites. For further
2 details, see text. For the bottom water and pore water data, see Appendix B.

| Site | Location | Year and cruise | Depth range cm | Diffusive Mn flux $\mu\text{mol m}^{-2} \text{d}^{-1}$ |
|------|------------------------|-----------------|-------------------|---|
| LF1 | Northern Gotland Basin | 2009 R/V Aranda | BW-0.25 | 115 |
| BY5 | Bornholm Basin | 2009 R/V Aranda | BW-0.5 | 236 |
| LL19 | Northern Gotland Basin | 2009 R/V Aranda | BW-0.25 | 81 |
| BY15 | Gotland Deep | 2009 R/V Aranda | BW-0.25 | 98 |
| F80 | Fårö Deep | 2009 R/V Aranda | BW-0.25 | 84 |
| LD1 | Landsort Deep | 2011R/V Pelagia | BW*-2.5 | ~220 |

3 * LD1 has no measured bottom water sample. Therefore, the flux was estimated using the
4 bottom water value from the Landsort Deep site BY31 from Mort et al. 2010.

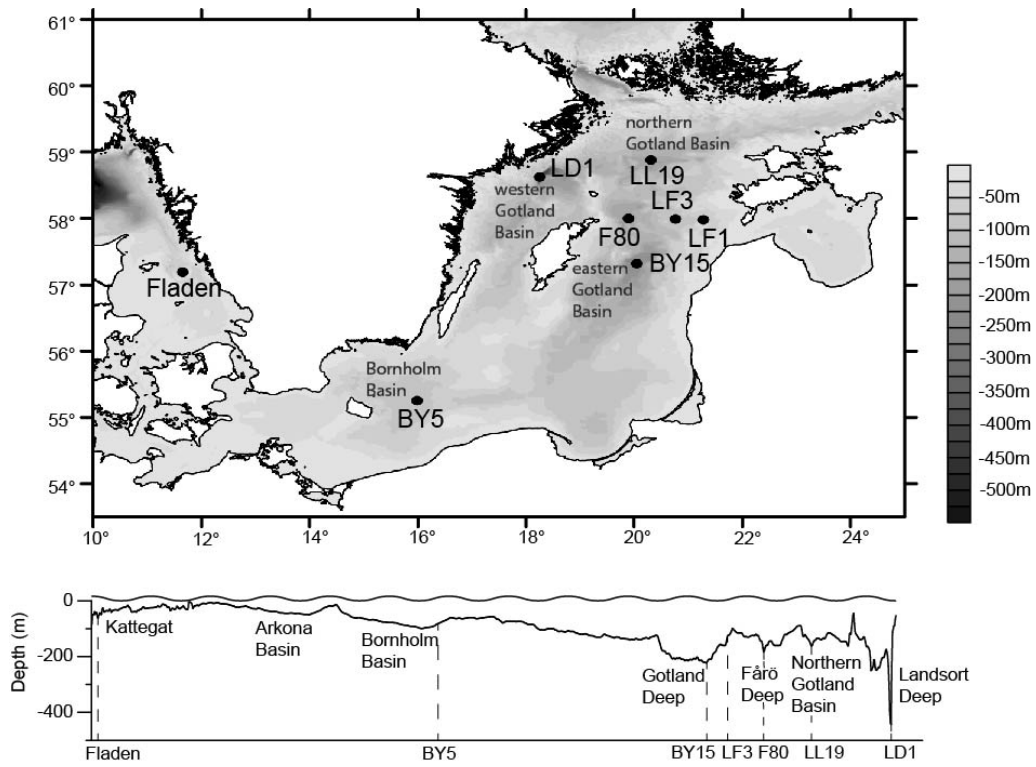
5

1 Table 3. Environmental parameters, boundary conditions (where $x=0$ refers to the sediment-
 2 water interface and $x = 1$ cm refers to a depth of 1 cm in the sediment) and first-order rate
 3 constants used in the simple diagenetic model for Mn for a “typical” Gotland basin sediment,
 4 including the sources, where relevant.

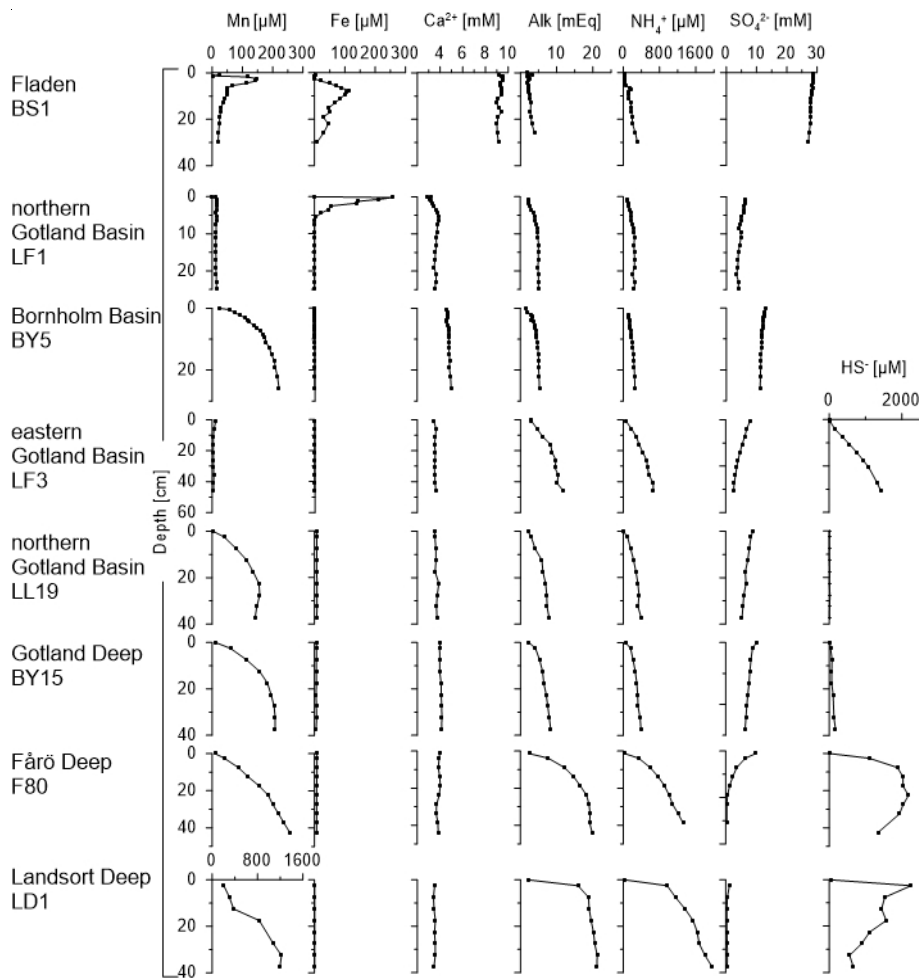
| Environmental and transport Parameters | Value | Source |
|---|-----------------------|--|
| - Porosity (vol%) | 99 | Appendix B |
| - Temperature (°C) | 5 | Appendix B |
| - Salinity | 12 | Table 1 |
| - Sedimentation rate (m yr^{-1}) | 0.0025 | Table 1 |
| Boundary condition at sediment water interface ($x=0$)* | | |
| Fixed concentration, Mn^{2+} (mol m^{-3}) | 0 | Typical for oxic waters |
| Fixed flux of MnCO_3 ($\text{mol m}^{-2} \text{y}^{-1}$) | 0 | Assuming all formation in the sediment |
| Transient flux of Mn oxides ($\text{mol m}^{-2} \text{y}^{-1}$) | 4 months: 1, then 0 | Section 4.1, 0.33 mol m^{-2} deposited in 4 months |
| Rate constants | | |
| - kred (yr^{-1}) | Range of 0.1 to 1,000 | Slomp et al (1997) & Wang & Van Cappellen (1996); see text |
| - kprec (yr^{-1}) | 5,000 | Wang & Van Cappellen (1996); see text |

5 *For all chemical species a zero-gradient boundary condition was specified at the bottom of
 6 the model domain.

7



1
 2 Figure 1 Bathymetric map and depth profile of the Baltic Sea showing the locations of the
 3 sampling sites.
 4

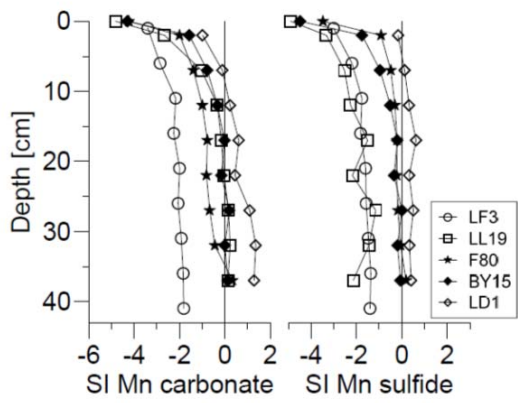


1
 2 Figure 2 Pore water profiles of dissolved manganese (Mn), iron (Fe), calcium (Ca), alkalinity,
 3 ammonium and sulfate for all 8 sites and hydrogen sulfide for the 5 deepest sites. Note, that
 4 dissolved Fe is below the detection limit in core LF3 and LD1 and dissolved sulfide is
 5 expressed as HS⁻, some H₂S can be present as well.

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Gelöscht: 2+

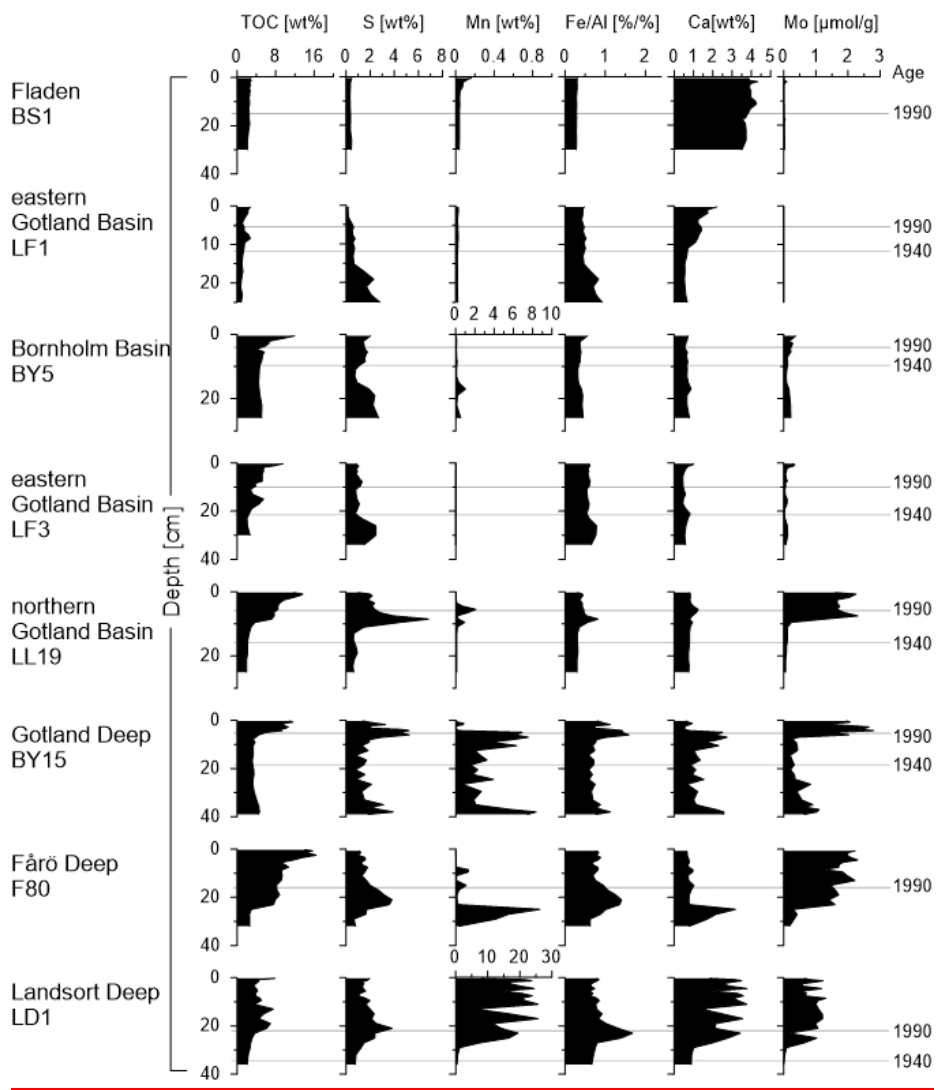
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1

2 Figure 3 Saturation indices (SI) for Mn carbonate (here as $Mn_{0.74}Ca_{0.26}CO_3$) and Mn sulfide as
 3 calculated from the pore water data with PHREEQC.

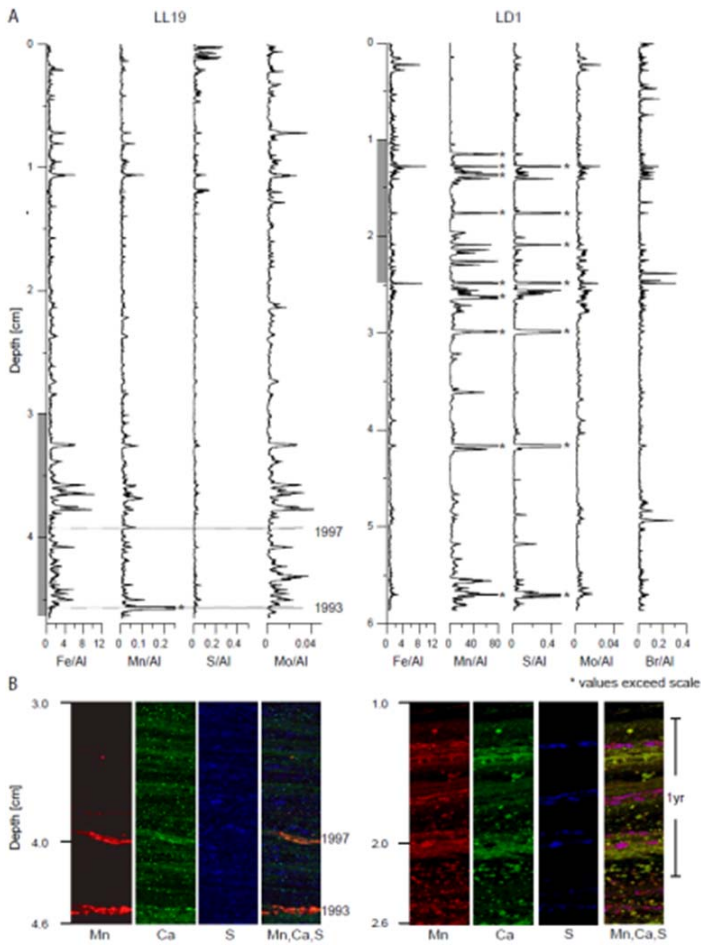
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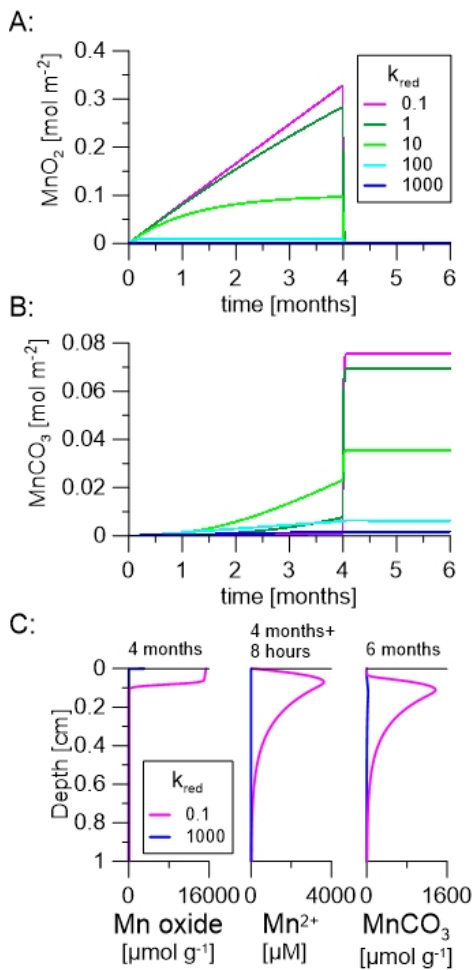
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2 Figure 4 Sediment depth profiles of total organic carbon (TOC), sulfur (S), manganese (Mn),
 3 iron to aluminum ratio (Fe/Al), calcium (Ca) and molybdenum for all 8 sites. Note the
 4 different scale for manganese at Fladen and LF1, and LD1. Grey lines indicate the years 1990
 5 and 1940, based on sediment dating. These date markers are used to demonstrate the
 6 variability of sedimentation rates in the study area.

7



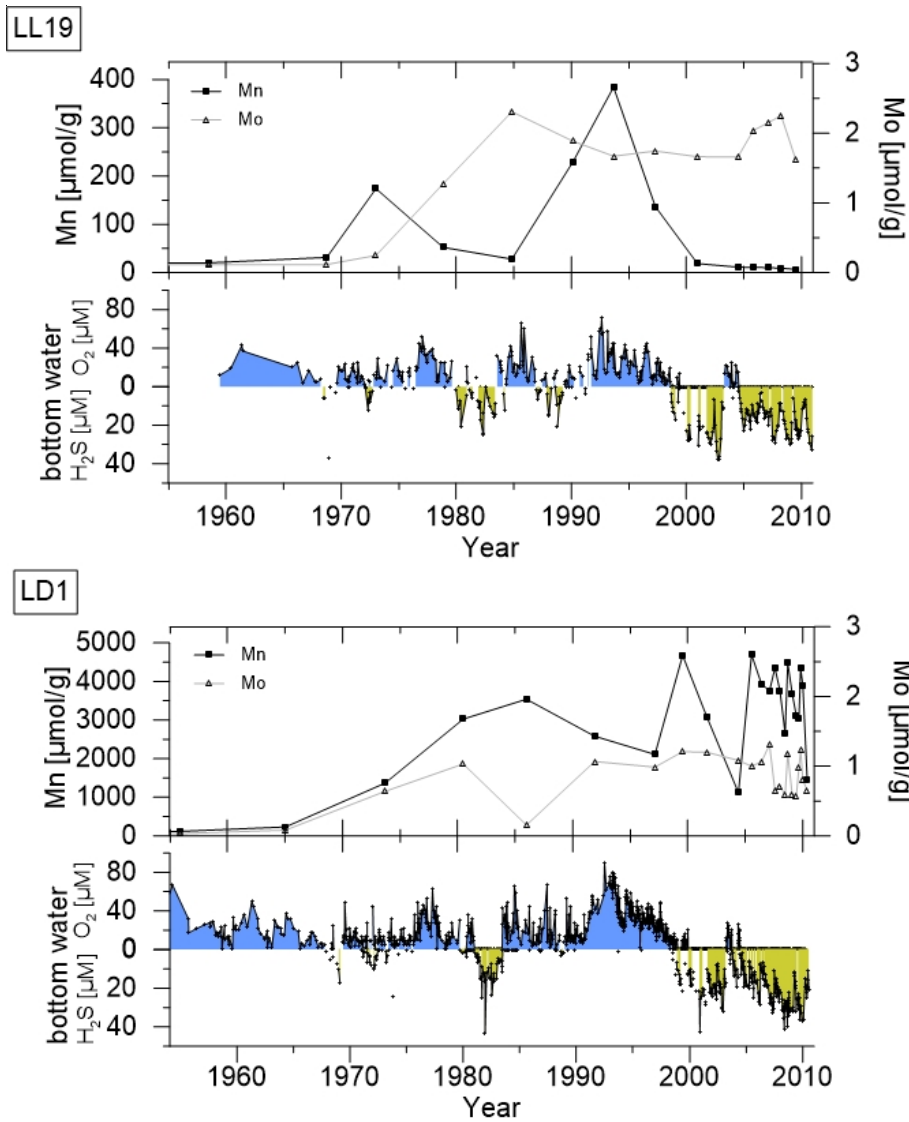
1
 2 Figure 5 A: High resolution elemental profiles of Fe/Al, Mn/Al, S/Al, Mo/Al and Br/Al (only
 3 LD1) generated by LA-ICP-MS line scanning for resin-embedded surface sediment blocks.
 4 Note the difference in absolute values for Mn/Al between LL19 and LD1. The depth scale
 5 refers to the compacted sediment in the resin blocks (the total length of wet sediment prior to
 6 embedding was 5.5 cm (LL19) and 11.3 cm (LD1)). Peaks marked with a * exceed the scale.
 7 B: Compilation of micro XRF maps for station LL19 and LD1 showing the distribution of
 8 manganese (red), calcium (green) and sulfur (blue) at the depth indicated by grey panels in the
 9 LA-ICP-MS line scans. Color intensity within each map is internally proportional to XRF
 10 counts, but relative scaling has been modified to highlight features. The fourth picture for
 11 each station shows a RGB (red-green-blue) composite of the three elements with orange to
 12 yellow colors indicating a mix of Mn and Ca, and therefore, representing Ca-Mn carbonates.
 13 The pink/purple represents a mix of Mn and S, hence Mn sulfide.



1
 2 Figure 6. A: Integrated amount of Mn oxide and B: Integrated amount of Mn carbonate in the
 3 upper cm of the sediment (in mol m⁻²) for the simulation with k_{red} being equal to either 0.1, 1,
 4 10, 100 or 1000 yr⁻¹ for the first 4 months and equal to 1000 yr⁻¹ for the last 2 months, as
 5 described in the text. C: Depth profiles of Mn oxide (after 4 months, end of the oxic phase),
 6 dissolved Mn (after 4 months and 8 hours, directly after the start of the anoxic phase) and
 7 MnCO₃ (after 6 months) as calculated with the model in the same scenarios as A and B.

8

- Gelösch: Total sediment-water exchange of Mn²⁺
- Gelösch: i
- Gelösch: rates
- Gelösch: formation over
- Gelösch: first 4 months (
- Gelösch:)
- Gelösch: and for the total 6 months (with k_{red})
- Gelösch: to represent anoxia during the last two months of each simulation)
- Gelösch: ²⁺
- Gelösch: at the start of the anoxic phase



1
 2 Figure 7 Records of sediment manganese and molybdenum for 1955-2010 for core LL19 and
 3 core LD1 and corresponding bottom water oxygen and sulfide concentrations from
 4 monitoring data (for LD1 the nearby monitoring station LL23 was used; ICES Dataset on
 5 Ocean Hydrography, 2014).