

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.”*

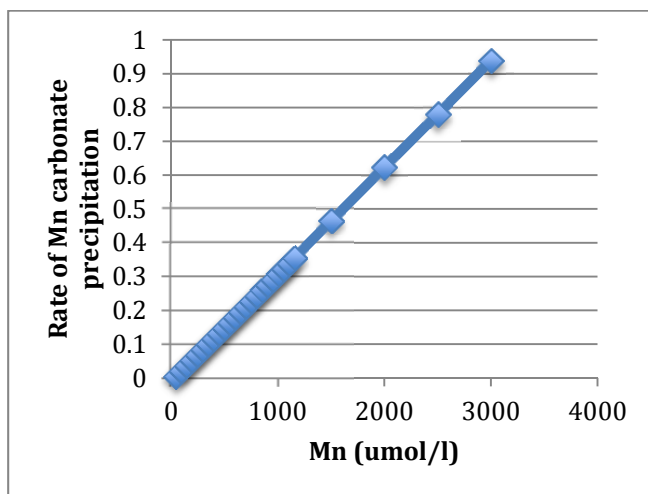


Figure R1. see reply to point 21.

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.