Utrecht, May 12, 2015

Dear Prof. Fennel,

Thank you for the opportunity to submit a revised version of our manuscript.

So far, 5 reviewers have assessed two versions of this manuscript, with three being very positive and supportive of publication (minor revisions) and two being rather negative (rejection). In response to the editorial request to address the comments of all reviewers and especially the most critical ones, we include our answers to all 5 reviews in our reply, expanding and modifying our earlier responses where necessary. We start with the most recent reviews (#4 and #5), followed by the earlier ones. For easy reference, we have now also numbered all the points raised by each reviewer.

With our revised manuscript, we have now submitted a more extensive supplementary data file, also including data that was already published in earlier papers.

Many aspects of the Mn cycle in marine sediments are still incompletely understood. This may explain the widely diverging views of the reviewers regarding our paper. In our revision, we have done our best to address all issues raised. In most cases, we adjusted the text and figures as suggested. Where we did not agree with the reviewers, or where the reviewer's suggestions were in conflict with each other, we have provided detailed arguments in our reply letter to clarify our position and have in all cases also modified the manuscript either by removing the text or adding further explanations. We have now also more clearly identified what interpretations are brought forward as hypotheses. Finally, we have also added the results of a diagenetic model for Mn demonstrating that the mechanism that reviewer #1 questions is in fact feasible. We hope that the diverging opinions on the interpretation of our data do not preclude publication. We believe an open debate in the scientific literature is critical in bringing the field forward.

Sincerely, on behalf of all co-authors,

Conny Lenz

## Content

## Response to reviewer #4 (rejection, on 1. revised version)

The purpose of the present study is to characterize processes of Mn enrichment in Baltic Sea sediments according to recent changes due to expanding hypoxia since the 80s. I am not familiar with the specific physical and environmental processes that take place in the Baltic Sea. Therefore my review will focus on biogeochemical processes and data described in this manuscript.

First of all, I was struck by the lack of some data and calculations to support the conclusions and by the lack of some alternative explanations that could also explain the data. This is detailed below.

1. The sediment characteristics are not given : is the grain size constant? what is the profile of porosity? These parameters are needed to verify the flux calculation. The grain size of the different stations is a relevant piece of information to compare the stations. If the grain size changes within a vertical profile, the story is no more the same.

All sediments are fine-grained and there are no major changes in grain-size with depth in the sediment. We now have included all porosities (calculated from the water contents) in the supplementary data file, also those that were already published previously (see Jilbert et al., 2011). The porosity of the surface sediment was used to calculate the benthic flux. We also have included the total Al contents for the sediment (a proxy for clay content) in the appendix.

The text has been modified as follows:
page 5, line 3: “*Fine-grained sediments from 8 locations… .*”
page 12, line 13: “*Sediments are highly porous (Appendix B) and rich in organic carbon… .*”
page 12, line 17-18: “*High contents of total Al, which are a proxy for clays, are in line with the presence of fine-grained sediments throughout the cores (Appendix B).*”

2. Some pore water and solid fraction data are lacking : how can the authors calculate the saturation index of a Mn-Ca carbonate without dissolved Ca2+ data?

We used the measured $Ca^{2+}$ concentrations in the porewater in our calculations. The Ca analyses are now included in the methods and we include the $Ca^{2+}$ profiles in Figure 2 and the supplementary data file (Appendix B). We now also describe the $Ca^{2+}$ profile in the Results.

3. The redox geochemistry of Mn depends on the geochemistry of several electron donors or acceptors, such as carbon species, nitrogen species, oxygen, sulphur species, and iron species. Here, we have an interesting collection of data that includes high vertical resolution profiles of dissolved Mn, solid Mn, TOC, dissolved ammonium, particulate S and Mo, dissolved sulphate and sulphide, and alkalinity. Some samples of bottom water data are lacking (sulphate in Landsort Deep).

We indeed regretfully lack a bottom water measurement for sulfate for the Landsort deep. However, this does not in any way impact or invalidate any of our results or conclusions.

4. Nothing about iron species. However, it is well known that Fe2+ is a reducing compound for Mn-oxides. LD1 site Nothing about methane. Methane is probably a key parameter in the Landsort Deep, where the TOC content is very high and sulphate is close to zero. Methane is a reducing agent for Mn and Fe-oxides; methanogenesis may have a control on CO3 content (i.e. on solid carbonate stability). I am quite convinced that some iron (and maybe methane) data have been obtained by the authors. Did they attempt to publish these data in another paper? If these data exist, they must be included in the present study. If they do not exist the data set is incomplete and the conclusions given here are not valid.

Dissolved $Fe^{2+}$ profiles for all sites except the Landsort Deep LD1 site were published previously (see Jilbert et al. 2011). Dissolved $Fe^{2+}$ is extremely low in porewaters of anoxic basins because of the abundant presence of sulfide.

We now have added the dissolved $Fe^{2+}$ profiles in Figure 2 and the data are included in the supplementary data file (Appendix B).

We also have added two sentences describing the profiles in the results (page 11, line 22-23: "*Pore water $Fe^{2+}$ shows a subsurface maximum at the Fladen and LF1 sites, but is low or absent in the porewater at all other sites.*"

The role of methane as a reductant for Mn and Fe oxides is still highly debated in the literature because the micro-organisms responsible for the reaction have not yet been identified and all evidence so far is indirect and not 100% conclusive. Additionally, if the process indeed takes place, it is a relatively slow reaction (see Beal et al., 2009 and Egger et al., 2015) and it is highly questionable whether it would be more important than the reaction of Fe and Mn oxides with sulfide, which is so abundant in the water column of these basins in between inflow events. While we indeed measured methane at the LD1 site, significant degassing occurred during sampling and we do not believe our measured methane profile for this site represents actual methane concentrations. For completeness, we have added the $CH_4$ profiles for all four deep basin sites in Appendix B and include a statement regarding the degassing at site LD1. We also now include the description of the methane sampling and analyses in the manuscript.

To address the reviewer's comments, we now have added in the manuscript that $Fe^{2+}$, $CH_4$ and $NH_4$ (see the later comment) are also potential reductants for Mn oxides. We also explain why a change in the availability of these constituents is unlikely to explain the recent changes in Mn sequestration observed in the deep basin sediments of the Baltic Sea. The revised text (page 20 line 15 and further) reads as follows:

*"Alternatively, we hypothesize that the Mn oxides that are formed following modern inflow events might be reductively dissolved faster than previously. As a consequence, the* $Mn^{2+}$ *released from the oxides could then escape to the overlying water instead of being precipitated in the form of Mn carbonate. This is in line with the results of the simple diagenetic model where high rates of Mn oxide reduction lead to less Mn carbonate formation (Figure 6).*

*There are multiple possible reductants for Mn oxides in marine sediments, including sulfide,* $Fe^{2+}$ *(e.g. Canfield and Thamdrup, 2009),* $NH_4^+$ *(e.g. Luther et al., 1997), and* $CH_4$ *(Beal et al., 2010), with the role of the latter two reductants in marine sediments still being debated. Because* $Fe^{2+}$ *and* $CH_4$ *concentrations in the porewaters of the surface sediments of the Gotland basin area are negligible, these constituents are unlikely to play an important role as a reductant for Mn oxides in the northern Gotland basin (LL19), Fårö Deep (F80) and Gotland Deep (BY15) sites. Furthermore, there is no evidence for a major recent change in porewater* $CH_4$ *concentrations in the surface sediments. There is evidence, however, for a recent rise in the bottom water sulfide concentrations in the deep basins of the Baltic Sea (Figure 7) linked to eutrophication (Carstensen et al., 2014). As shown for the northern Gotland Basin site (LL19), the more persistent presence of high concentrations of bottom water sulfide and enrichments in sediment Mo, coincide with the decline in Mn in the sediment (Figure 7).*

*We hypothesize that Mn oxides that are formed following modern inflow events and that are deposited on the seafloor (Heiser et al., 2001) are no longer being converted to Mn carbonates because of higher ambient concentrations of sulfide in the bottom water and in the porewater. These higher sulfide concentrations are likely the direct result of increased sulfate reduction driven by the ongoing rise in productivity in the Baltic Sea (Gustafsson et al., 2012). The observed decline in Fe/Al at our deep basin sites (Figure 3) suggests more muted shuttling of Fe oxides from shelves to the deeps linked to the expanding hypoxia (e.g. Scholz et al., 2014) which have may reduced the buffer capacity of the sediments for sulfide (e.g. Diaz and Rosenberg, 2008).*

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

$$R = kC_{TS}C_{Mnoxides} \qquad (6)$$

*where k is a rate constant and $C_{TS}$ stands for the total sulfide concentration, i.e. the sum of the concentrations of $H_2S$ and $HS^-$. In our modeling approach, the rate law for this process is assumed equal to*

$$R = k_{red}C_{Mnoxides} \qquad (7)$$

*Thus, if sulfide is the reductant, $k_{red}$ can be assumed to be equivalent to the product of k and $C_{TS}$. Given that sulfide will be absent in oxygenated porewaters, i.e. can be below 1 $\mu$M in the surface sediment, but also can range up to 1.1 to 2.2. mM as observed at sites F80 and LD1 (Figure 2; Appendix B). Thus, $k_{red}$ values for surface sediments in the Baltic Sea are expected to range over at least 3 to 4 orders of magnitude, as assumed in our model calculations. In our model Mn carbonate formation is found to critically depend on the value of $k_{red}$ (Figure 6). This provides support to our suggestion that a recent rise in sulfide concentrations in the porewaters and bottom waters may have made the surface sediments more hostile to the preservation of Mn oxide after an inflow and might contribute to their reduction. More $Mn^{2+}$ could then escape to the overlying water instead of being precipitated in the form of Mn carbonate, explaining the lack of recent Mn enrichments."*

5. Some simple mass balance calculations could support, confirm, or invalidate some hypothesis presented in the paper.

We have modified and expanded the quantification. For further details see points 18 and 22 below. We also added calculations with a simple diagenetic Mn model in sections 2.7, 3 and 4.3 to demonstrate that an increase in reduction rates of Mn oxides linked to more porewater sulfide as a result of ongoing eutrophication could explain the observed decline in Mn carbonate formation.

Detailed comments :

6. First sentence of the introduction : "Manganese (Mn) enrichments in sedimentary deposits are often used as an indicator of redox changes in the overlying waters" is not valid. Write "could be" instead of "are often", because Mn-rich deposits have been used for other purpose, such as sedimentary source (in the arctic), sedimentary processes (contourite, turbidite), which have nothing to do with changes in the redox state of the water column.

We changed *"are often used"* to *"can be used".*

7. Introduction : p2, line 17 : Mn-enrichment in permanently anoxic water also occurs in some hydrothermal settings (e.g. brine-filled deeps in the Red Sea)

We are aware of the excellent work on Mn in brine-filled basins in the Red Sea by Anschutz et al. (1995) and others. However, hydrothermal brine pools are very different from brackish/marine systems and mentioning them could in our view lead to confusion about the environments we are focusing on. To address this reviewer's comment, we now make clear that we are restricting ourselves to brackish/marine systems by adding this specifically on page 2 line 14: *"Manganese (Mn) enrichments in brackish and marine sedimentary deposits can be used."*

8. Introduction p2 line 25 : Mercone et al 2001 is not an appropriate reference here, since it refers to sapropel deposition (which includes anoxic events)

We refer the reviewer to page 32 and further of the Mercone et al. paper where the two Mn peaks at the top of the sapropel are explained: *"The mechanism for the formation of the two Mn/Al peaks in both cores is therefore interpreted as being related to times when oxygen levels increased in the bottom waters*" and *"it is unlikely that the Mn peaks can be stable at present as Mn oxyhydroxides"...."the presence of kutnahorite in the samples is also confirmed by…"* Thus, it is an appropriate reference for input and precipitation of Mn oxides and transformation to Mn carbonate during burial.

However, to avoid confusion, we have removed the reference.

9. Introduction p2 lines 29-30 : "The Baltic Sea provides an ideal environment for studies of redox-dependent Mn dynamics because of the large spatial and temporal variations in oxygen conditions over the past century" I am not sure that a place that experiences so many changes is an "ideal" environment to try to understand the Mn-redox behaviour, apart from when all the needed parameters are provided, which is not the case here.

We rephrased this sentence to (page 3 line 7-11)*: "Redox-dependent dynamics of Mn have been studied extensively in the Baltic Sea (e.g. Huckriede and Meischner, 1996; Lepland and Stevens, 1998; Neumann et al., 2002) and are of interest because of the large spatial and temporal variations in oxygen conditions over the past century, that are particularly well documented since the 1970's (Fonselius and Valderrama, 2003)."*

10. Introduction p3 line 18 : see the work by Mouret et al 2009 (Benthic geochemistry of manganese in the Bay of Biscay, and the sediment accumulation rate. GeoMarine Letters 29:133–149) that describes the relationship between Mn-inventory in sediment and the sediment accumulation rate

We are not certain why the reviewer is referring to this (very interesting) paper here. We are describing the Mn shuttle here, not the link between Mn inventory and sediment accumulation rates. We now include a citation of the paper earlier (page 3 line 28) in the same paragraph *"…and contribute to the depositional flux of Mn oxides (Mouret et al., 2009), or may be …."*

11. Methods p5, lines 25 and 28 : do you mean 0.3 and 0.125 g (not mg)

We have made the correction.

12. Methods p5, line 29 : What about AVS? during acid attack, you may have lost sulphur from AVS, which is probably a major fraction of particulate S.

This is a standard and well-tested method to measure the total elemental composition, including total S, of sediments. During the sample handling prior to the destruction, the samples are exposed to the atmosphere. Thus all AVS will already oxidize and will not be lost upon acidification. We have now added a reference for the method (Passier et al., 1999) which has been used in our lab for these types of analyses for decades.

13. Methods : p6 line 3 and appendix1 : age model. The age model is valid only if the sediment is homogeneous (sieved sediment or sediment with initial constant grain size). Data of mass accumulation rate (appendix) can be validated only if the authors provide the porosity or the water content data.

See previous reply to comment 1, all sediments were fine-grained and the porosities are now included (Appendix B).

14. The appendix shows a column named "Observed 210Pb activity(mBq g-1,salt corr.)" with values that are very different from initial data. This must be explained.

We have now added the salt data in the table and a sentence in the caption of Table A1 to indicate that *"salt corr"* refers to the correction of the sediment weight for the salt content of the porewater.

15. section 2.6 : saturation states : Ca2+ data not shown;

See reply to comment 2 above. Now included.

16. pH data probably with an error (because of centrifugation, filtration) : this must be corrected or explained. A small error in pH change considerably the carbonate ion activity calculated with PHREEQ

Any ex-situ method to determine pH in porewaters will lead to an error. To our knowledge, there is no method to correct for this effect. Despite the potential error involved, pH measurements from centrifuged samples (e.g. Deng et al., 2010; Heiser et al., 2001) and samples collected from squeezers (e.g. Böttcher et al., 1998, Ocean Drilling Program Volume 160) are frequently reported and used in calculations of the saturation state of porewaters.

We had previously added a comment regarding the possible impact of degassing on ex-situ pH measurements on page 6 line 8-9 in the methods: *"Note that degassing of $CO_2$ may impact ex-situ pH measurements and may lead to a rise in pH".*

We now have further expanded the text in the results section as follows (page 12 line 4-8): *"Note that degassing of $CO_2$ during centrifugation may have led to a shift in pH to higher values, thereby enhancing the degree of saturation with respect to carbonate and sulfide minerals. However, an upward shift of ca. 0.5 pH units due to this effect would not greatly affect the observed trends with depth and contrasts between stations in the calculated saturation states presented."*

As indicated in the discussion, we find similar trends in the saturation state with depth as observed in previous studies where the pH was measured by directly inserting the electrode into the sediment on board ship (Carman and Rahm, 1997). Note, however, that the conditions that really matter for Mn carbonate mineral formation are those after a North Sea inflow as discussed in the text.

We have also added additional text in the methods (page 9 line 11-14) to explain the goal of our calculations:

*"Our calculations should be seen as approximations only with the main purpose of providing a comparison to previous calculations by Carman and Rahm (1997) and Heiser et al. (2001) to assess whether there are any indications for a change in saturation state of the porewater between inflows."*

We also have added the following text in the discussion (page 16 line 28-page 17 line 5) to make clear that the saturation state calculations refer to idealized minerals and that the saturation state following inflows is what matters most:

*"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 $Mn^{2+}$ 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)."*

17. p9, line 15-17 : "Mn is enriched in the surface sediment at Fladen, but is nearly absent at the LF1, BY5 and LF3 sites. At sites LL19, BY15, F80 and LD1, Mn is present again but is mostly observed at greater depth in the sediment. Sediment Mo is low at the Fladen, LF1, BY5 and LF3 sites…" Even if I read the manuscript carefully, I had difficulties to bring the sites symbols back to geographic sites. BY15, F80, LL19… should be changed by other names in the papers.

All the stations are monitoring stations with a long regular sampling history and their names are widely used in the literature. They cannot be omitted or changed. However, we have now added the geographical names besides the abbreviations in the manuscript where possible.

18. p11, line 11 : authors should provide the mass balance calculation : what is the

inventory in the water column? What is the bottom surface area located below the redoxcline? ...

Because the area of the bottom water below the redox cline varies with time, both on a seasonal and decadal time scale (Carstensen et al., 2014), and detailed data sets on $Mn^{2+}$ concentrations in the water column and Mn fluxes from the sediment are not available, an accurate calculation cannot be made. This is also what we wrote at the start of this paragraph (lines 3-9). We then took the approach to refer to calculations made by Heiser et al. (2001).

We now include a more explicit quantification and a more elaborate discussion of the available quantifications in the literature. We have also shifted the focus of this section to the role of inflows (as suggested by reviewer #5, see below). Page 14 following line 30 and following:

*"Due to the seasonal and inflow-related changes in redox conditions in the Baltic Sea, the lack of detailed data sets on $Mn^{2+}$ concentrations in the water column, and our very limited number of study sites, we cannot accurately estimate the different reservoirs of Mn and the importance of the present-day source of Mn from sediments overlain by oxic and hypoxic and anoxic bottom waters at the basin scale. Nevertheless, we will attempt to make a rough quantification using the data that is available and will then compare it to estimates from the literature.*
*Taking an average deep water volume of 2,000 $km^3$ and average hypoxic area of 47,000 $km^2$ (Carstensen et al., 2014) and a deep water concentration of Mn of 8 $\mu M$ (Löffler et al. 1997 as cited by Heiser et al., 2001), the amount of Mn in the deep water is estimated at $1.6 \times 10^{10}$ mol or 0.33 mol $m^{-2}$. The range in Mn fluxes in our study (0 to 236 $\mu mol\ m^{-2}\ d^{-1}$; Table 2) is comparable to benthic fluxes measured with in-situ chambers in other areas of the Baltic Sea (e.g. the Gulf of Finland; Pakhomova et al., 2007) and estimated from pore water profiles from the 1990's (e.g. Heiser et al., 2001). If we assume that a flux of ca. 90 $\mu mol\ m^{-2}\ d^{-1}$ is representative for the sediments overlain by hypoxic and anoxic bottom waters (Table 2; based on the fluxes for LL19, F80 and BY15), we calculate a yearly flux of 0.033 mol $m^{-2}$ from those sediments, which is equivalent to 10% of the inventory in the water column. In similar calculations, Heiser et al. (2001) estimated the amount of Mn in the Gotland Deep to be equal to 0.8 mol $m^{-2}$. With our estimate of the benthic flux, this would lead to a contribution of the benthic flux of less than 5%.*
*Note, however, that the role of the benthic flux of Mn from hypoxic sediments will vary spatially and may be biased towards high values because of preferential sampling of sites with a relatively high sediment accumulation rate in most pore water studies. This may explain the one order of magnitude lower benthic fluxes of Mn reported for the Gotland Deep area in 1999-2001 of ca. 7-8 $\mu mol\ m^{-2}\ d^{-1}$ by Neretin et al. (2003) when compared to those in our study (Table 2).*
*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). The exact impact of inflows on the oxygenation of the bottom waters in the deep basins of the Baltic Sea varies from site to site, however, and depends on the volume and oxygen*

*content of the inflowing water, its pathway and the oxygen concentration in the receiving basin (e.g. Carstensen et al., 2014), with the general flow of water in the deep basins going from the Gotland to the Fårö and the Landsort Deep (Holtermann et al., 2012). For example, the bottom water in the Gotland Deep was free of hydrogen sulfide for 4 months following the inflow of 1993-1994 (Neretin et al., 2003; Yakushev et al., 2011) whereas the Landsort Deep was less affected because the bottom water at the time contained oxygen already (Figure 7). Using biogeochemical modeling of a typical inflow in the Gotland Deep area, Yakushev et al. (2011) showed that dissolved $Mn^{2+}$ in the water column was oxidized to Mn oxides and settled to the bottom over a time period of months. Dissolved $Mn^{2+}$ appeared in the water column again upon the return of bottom water anoxia and steady state conditions in the water column were established in the model after ca. 1.5 years.*

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

*Notably, Yakushev et al. (2011) consider $Mn^{3+}$ besides $Mn^{2+}$ in their model for biogeochemical dynamics in the water column in the Gotland Deep. Dellwig et al. (2012) found recently that $Mn^{3+}$ is an important component in the water column Mn cycle in the Landsort Deep but not in the Gotland Deep. Further work is required to elucidate the potential importance of this finding to Mn dynamics in the Baltic Sea and its impact on other biogeochemical cycles (e.g. Pakhomova and Yakushev, 2013) and to determine whether $Mn^{3+}$ plays a role in the sediments as well and impacts Mn sequestration (e.g. Madison et al., 2011). Field studies of Mn dynamics in the water column and sediment during and directly after an inflow would be of particular value."*

19. p11, line 19-20. The conclusion given here are not supported by a quantitative discussion.

We have now revised this section of the discussion and include more quantitative details and have rephrased the conclusions. See reply to comment 18 and text above.

20. p12, discussion about Landsort Deep : The very low concentration in sulphate suggests that methane is present (probably in high amount). Author should explore the scientific literature that deals with lake biogeochemistry, because the sulphate depleted Landsort Deep sediments are like an organic-rich lake sediment. In the Landsort Deep CH4 represents probably a second source of organic C coming from below. This may have an impact on the whole benthic biogeochemistry.

See reply to point 4 above. We now address the potential role of $CH_4$ as a reductant for Mn oxides.

21. Authors claimed that there is a deep pore water source of dissolved Mn in the Landsort Deep because the concentrations of Mn are higher than in other stations. I would rather suggest that dissolved Mn2+ is controlled by the equilibrium with a carbonate in the other stations, whereas it is not controlled by the same solid phase in the Landsort Deep.

We have removed the deep source of dissolved Mn, see reply to point 22 below. We have added the formation of other minerals as a possibility (page 18, line 16-17)*: "The differences in pore water chemistry will also likely impact the exact solid phases formed in the sediments of the various deep basins."*

22. The pore water Mn concentrations are by far the highest at the Landsort Deep site (> 1 mM versus <0.26 mM of Mn2+). According to the authors, this "deep" diffusive supply of Mn to the surface sediment may in fact explain why the formation of Mn enrichments at this site is more continuous than at the other sites : A simple mass balance could be made to (in)validate this hypothesis : authors should compare the diffusive flux with the accumulation of authigenic Mn (based on sediment accumulation rate and Mn-inventory calculation)

We agree with the reviewer. We have now made the corresponding calculations and they show that the upward diffusive flux of Mn based on our porewater Mn profile is insufficient to explain the strong enrichments in sediment Mn in the Landsort Deep. We therefore have removed this from the manuscript. We now only refer to the role of Landsort Deep as an excellent sediment trap for Mn oxides, which we already mentioned but had given second place. The revised text now reads as follows: (page 18 line 4 and following)

*"However, the pore water $Mn^{2+}$ concentrations at Landsort Deep are much higher than elsewhere (> 1 µM versus <0.26 mM of $Mn^{2+}$). This may be related to the fact that the Landsort Deep is the deepest basin in the Baltic Sea and its geometry makes it an excellent sediment trap. As a consequence, sediment deposition rates are much higher than in the other Deeps (Lepland and Stevens, 1998; Mort et al., 2010). Results of the recent IODP expedition suggest that deposition rates may even be more than a factor of 6 higher (Expedition 347 Scientists , 2014). Sediment focusing is also expected to lead to a higher input of Mn oxides to this basin. Given that rates of mineral dissolution are expected to depend on the amount of material present, corresponding rates of input and dissolution of Mn oxide minerals in the sediment are likely higher in the Landsort Deep than at other sites. Thus, we suggest that differences in focusing of the sediment may explain the observed differences in pore water chemistry and Mn sequestration. The differences in pore water chemistry will also likely impact the exact solid phases formed in the sediments of the various deep basins."*

The *"deep source"* is also removed from the abstract, discussion and conclusions and now we refer to this difference in input:

Revised text: Abstract (page 1 line 25-28)*: "In the Landsort Deep, in contrast, Mn carbonate and Mn sulfide layers form independent of inflow events, which is possibly due to the much larger and continuous input of Mn oxides linked to sediment focusing."*
Section 4.4 (page 22 line 15-19): *"Our results for the Landsort Deep suggest that Mn enrichments may also form frequently in an anoxic basin as Mn carbonates and sulfides if the input of Mn from the surrounding area is exceptionally high due to sediment focusing. Mn enrichments in geological deposits thus can be indicative of both oxic and anoxic depositional environments, emphasizing the need for multiple redox proxies. "*
Conclusions (page 23 line 1-4): *"are still being precipitated. This could be due to strong focusing of Mn rich sediment particles and high rates of sediment accumulation in the Landsort Deep. Our results indicate that sediment Mn carbonates in the other deep basins of the Baltic Sea no longer reliably and consistently …."*

23. p. 13, line 21 : what do the authors means with "the most euxinic periods". Is it the periods with the highest S(-II) concentrations?

Yes, that is what we mean. We have now rephrased the text (page 19 line 9): *"coinciding with periods with the highest sulfide concentrations".*

24. H2S concentration in the figures are showed as negative oxygen concentrations. Here the real S(-II) data should be showed, in order to a avoid to add complexity in the manuscript.

We have made the suggested change.

25. p. 14 line 13 "But what can inhibit the formation of these Mn carbonates?" the simplest explanation is not put forward here : the upper sediment is not enriched in Mn-carbonate, because this part of the sediment pore water is undersaturated with respect to a carbonate phase (see the fig. 3). The saturation is reach only below 10 cm depth approximately in these stations.

The results of Figure 3 do not reflect conditions after an inflow when Mn carbonates are expected to form. To clarify this further, we have now expanded the text (page 20 line 4-6): *"After an inflow, supersaturation with respect to Mn carbonates is thus expected to be reached in the surface sediment and not only at depths below ca. 5-10 cm (Figure 3)."*

26. other hypothesis : high Fe2+ concentration at the sediment-water interface that prevent the accumulation of Mn-oxide (but Fe data are lacking)

See above. $Fe^{2+}$ concentrations are typically below detection because of the abundant sulfide. We now explicitly address this in the text (see response to point 4).

27. NH4 data are presented here. However, there is no discussion concerning the

role of NH4 as a reducing compound for Mn-oxide, despite the abundant literature on this topic.

We have included this possibility but have no indication for a recent major change in the $NH_4$ concentrations in the porewater needed to explain this. See reply to point 4 above.

28. P. 15 conclusion : first sentence : this conclusion must be corroborated by a mass balance calculation.

We have removed this conclusion.

29. conclusion p15 lines 25-28 :" We show that the most recent sediments in the Fårö Deep and Gotland Deep contain low concentrations of Mn near the sediment surface. We postulate that this is due to the expansion of hypoxia over the past decades with the Mn oxides formed during inflows from the North Sea often being reduced so rapidly that the Mn2+ is lost to the water column."
This text suggests that the Mn content is not simply low, but that is it lower than what it should be. However nothing in the ms support this conclusion. Low concentration of Mn in anoxic surface sediment is very common.

We refer the reviewer to section 4.2 (page 11, lines 23 and further; previous manuscript version) where we wrote *"Formation of Mn bearing carbonates in the Gotland Basin and Landsort Deep is generally described as being ubiquitous (e.g. Jakobsen and Postma, 1989)".* We also explain the mechanism suggested to be responsible for the formation of those Mn carbonates in detail and how specific accumulations of Mn carbonate are directly correlated to inflow events and include appropriate references. Indeed, low Mn in anoxic surface sediments is common in other systems, but, until recently, was not common in the surface sediments of the deep basins of the Baltic Sea.

We now mention this in more detail in the introduction of the manuscript and in section 4.2:

Revised text in the introduction (page 4 line 9-11): "*If release of dissolved $Mn^{2+}$ from Mn oxides - formed at the sediment surface following inflows of oxygenated North Sea water - is the dominant control for Mn carbonate formation in the sediment as suggested for the Gotland Deep….*"

Revised text in Section 4.2 (page 16 line 27 and following): *"Formation of Mn bearing carbonates in the Gotland Basin and Landsort Deep is generally described as being ubiquitous after inflows (e.g. Jakobsen and Postma, 1989). 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 $Mn^{2+}$ concentrations in the porewater 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).”*

30. conclusion p15 line 31 : “Our results indicate that sediment Mn carbonates in the Baltic Sea no longer reliably record inflows of oxygenated North Sea water.” the “no longer” suggests that Mn carbonates reliably recorded inflows in the past. This has not been demonstrated here, nor presented in the introduction based on literature.

See reply to point 29 above.

31. Tabl 1 : oxygen concentrations given in mL/L. Please use molar units

We have made the suggested change.

## Response to reviewer #5 (minor revisions, on 1. revised version) P.L. Croot

Overview:
1. This manuscript presents data from studies into the sediment chemistry from a series of stations in the Baltic Sea with a focus on Mn and its potential as a tracer of oxygenation events in the anoxic deep waters. The experimental approach is very strong, well described, and state of the art and the article is well written to the point and concise.

We thank the reviewer for the compliments.

2. The authors interpret their dataset in terms of differing modes for Mn carbonate formation in the sediments in response to periodic injections of oxygenated waters into anoxic deep waters. In the Gotland deep they suggest that MnCO3 previously formed from MnO2 that was precipitated following North Sea inflows, but now is absent as the anoxia is now basin wide. While in the Landsort Deep, MnCO3 and MnS form independent of inflow events as there is a deep pore water source of reduced Mn. These findings have important implications in terms of paleo reconstructions of oxygenation events. However at present the paper lacks an appreciation of the time scales involved nor the potential for other controlling processes (e.g. pyrite formation and/or basin shape/size) and how this impacts the Mn inventories and concentrations in the bottom waters and porewaters.

We have now included results of a simple diagenetic model for Mn to demonstrate the possible time scale of the processes in the sediment related to Mn oxide dissolution and Mn carbonate formation. See response to Reviewer #4, point 5. While Mn indeed can be incorporated in pyrite, the amounts are relatively minor when compared to those present in Mn carbonate, as we showed in a previous study for Baltic Sea sediments (Lenz et al., 2014). We now explicitly mention this in the manuscript (page 2 line 29-32): "*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).*"

The shape/size of the basin has not changed, but the area of the hypoxic and euxinic area has. This is now mentioned not only in the main text, but also in the conclusions (see response to detailed comments below).

3. There is a frequent referral to a potential recent change in that the generation of H2S after an oxygenation event is faster now but no explanation is given of how this can occur.

Now included in the text and demonstrated with a diagenetic model. See response to reviewer #4, point 5.

4. What would be most useful however is some sort of description or evaluation (model or otherwise) of what the tipping point is for a record of an oxygenation event to be recorded. For instance if there is a short interval between oxygen events is it recorded as one or two events, alternatively if there has been no event for several years and sulfide has built up appreciably, how big an event has to occur for it to be recorded in say either the Landsort or Gotland basins?

We agree with the reviewer that this would be very interesting. However, the data set is too limited to allow the identification of such a tipping point for the water column. We now include a more detailed discussion of the results of the modelling study of Yakushev et al. (2011) on the dynamics of Mn in the water column following an inflow, see response to points 5 and 18 of reviewer #4. We clarify in the text that the suggested role of sulfide is brought forward as a hypothesis and we demonstrate the sensitivity of the formation of Mn carbonate in the sediment to the rate of reduction of the Mn oxides directly following an inflow using a diagenetic model.

Overall though this manuscript should be acceptable after moderate revision as outlined below.

General Comments:
5. Timescales of response to an oxygenation event:
One aspect that is poorly explored in the manuscript at present is how quickly the system responds to an oxygenation event and how quickly does it return to the previous state. Laboratory data indicates that MnS is apparently oxidized rapidly when re-suspended in oxygenated seawater (Simpson et al., 1998; Zhang and Millero, 1994) and may form MnO2 or even Mn(III) species. Simple abiotic oxidation of Mn(II) is very slow (von Langen et al., 1997) but is accelerated by bacteria (de

Vrind et al., 1986; Sujith and Bharathi, 2011; Tebo and Emerson, 1986; Tebo, 1991; Tebo et al., 2005).
There are also works that look at the kinetics of reduction of MnO2 by H2S (Yao and Millero, 1993) and this information would be useful for looking at the timescale that is involved on that side of the redox cycle.

This is now discussed in section 4.1, see response to point 4 of this reviewer. We now refer to the work of Wang and Van Cappellen (1996) in our discussion of Mn oxide reduction by sulfide. The modeling now provides insight in the net result of diffusion, reduction and precipitation in the sediment

6. Reactive Mn, Mn(III) in the Baltic:
A difference in reactive Mn between the Gotland deep and Landsort deep has been commented on recently in another work (Dellwig et al., 2012). In their study they found almost no reactive Mn, thought to be Mn(III) species, in the Gotland deep. While in the Landsort deep there was a strong gradient of increasing reactive Mn towards the central part of the basin. These authors suggested lateral intrusions of oxygen into Gotland deep prevented the formation of stable suboxic zone where reactive Mn could accumulate. It would be useful to discuss then the potential for reactive Mn to impact the formation of MnCO3 etc as presumably an oxygenation event may lead to an increase in Mn(III) within the sediments (Luther III et al.; Madison et al., 2011; Oldham et al.; Trouwborst et al., 2006) that may be supported by organic complexing agents found there.

We agree that Mn(III) could potentially be important and we now include this in section 4.1 (page 16 line 17-25).

*"Notably, Yakushev et al. (2011) consider $Mn^{3+}$ besides $Mn^{2+}$ in their model for biogeochemical dynamics in the water column in the Gotland Deep. Dellwig et al. (2012) found recently that $Mn^{3+}$ is an important component in the water column Mn cycle in the Landsort Deep but not in the Gotland Deep. Further work is required to elucidate the potential importance of this finding to Mn dynamics in the Baltic Sea and its impact on other biogeochemical cycles (e.g. Pakhomova and Yakushev, 2013) and to determine whether $Mn^{3+}$ plays a role in the sediments as well and impacts Mn sequestration (e.g. Madison et al., 2011). Field studies of Mn dynamics in the water column and sediment during and directly after an inflow would be of particular value."*

7. It should also be noted that there is now considerable Mn data from the Baltic (Dellwig et al., 2012; Kashiwabara et al., 2009; Neretin et al., 2003; Pakhomova and Yakushev, 2013; Pohl and Hennings, 2005; Yakushev et al., 2009) which illustrate that Mn in the anoxic waters in the Baltic can vary appreciably due to the oxygenation events and this needs to be taken into account. The recent work by Pakhomova and Yakushev (2013) is a good place to start as they provide a minor compilation of values and a modelling effort. In this context the recent works on Mn cycling at the redoxcline in the Baltic (Dellwig et al., 2012; Schnetger and Dellwig, 2012) should also be included in the discussion as during an oxygenation event in

the deep waters the same sub-oxic chemistry will be brought into play in the sediments.

We have revised section 4.1 to include a more elaborate and quantitative description of water column dynamics of Mn, see response number 18 to reviewer #4. We already cited most of the papers listed above but now also cite Pakhomova and Yakushev (2013). The sedimentary Mn cycle is discussed in relation to the results of the diagenetic Mn model.

8. Mn incorporation into pyrite:
One aspect of Mn chemistry in anoxic environments that appears to be under explored here but could be a key pathway is the earlier finding that dissolved Mn can adsorb onto FeS phases and be pyritized (Morse and Luther III, 1999). These authors found that Mn was more readily incorporated into pyrite when the degree of pyritization (pyrite Fe/(pyrite Fe + reactive Fe) was above 40%. Thus the coexistence of Mn and S in the sediments may also be related to FeS availability and not MnS formation per se. In this case the ratio of Fe to Mn, the degree of pyritization, as well as the sulfide concentration would be important. Pyrite has already been shown to be an important species for transferring Fe to the sediments in the Gotland deep (Fehr et al., 2010). Information on the pyrite and Fe(II) content in the sediments/porewaters would also then help to gauge if this was having an impact on the Mn cycle.

This plays a minor role only. We now mention this in the manuscript. See reply to point 2.

9. The age of Baltic seawater and mixing in the Gotland Basin:
One of the major themes of this paper is the influx of oxygenated water into the different basins of the Baltic. It would therefore be of interest to link the present work with some recent physical oceanographic studies of the water mass age in the Baltic (Meier, 2005) and the Baltic sea mixing experiment BATRE (Holtermann and Umlauf, 2012; Holtermann et al., 2012). In the latter an inert tracer (SF5CF3) was injected into the Gotland Basin at 200 m depth and followed over 18 months or so. BATRE is useful in the present context as it points to the role of typography in the mixing of the bottom waters in this region and to the potential response time of an oxygenation event.

We have now included more information on the inflows in the discussion and include more references, see previous replies, including a reference to the work of Holtermann et al., 2012 (page 15 line 31). We also provide more quantitative details on the area and volume of the deep water that is anoxic and we now refer to the water transport from the Gotland to the Faro to Landsort Deep. See reply to point 18 of reviewer #4 above.

10. Mn carbonate formation and solubility:
There are a number of other recent works that have looked at the formation and

solubility of Mn carbonates in seawater (Jensen et al., 2002; Johnson, 1982; Luo and Millero, 2003; Neher-Neumann, 1994; Radha and Navrotsky, 2014; Wartel et al., 1990). Note that there are also papers that deal with the transformation of aragonite/calcite to Mn carbonate (Böttcher, 1997; Böttcher, 1998) and this pathway should be mentioned also in the discussion along with data on the carbonate system in the water column (Schneider et al., 2010; Ulfsbo et al., 2011). This would then help to make the case that MnCO3 formation is only occurring in the uppermost part of the sediments.

The Baltic Sea differs from other systems that there are very few calcifiers in the water column, i.e. transformation of biogenic calcite or aragonite is not relevant here. None of the previous papers regarding Mn carbonate formation in the Baltic Sea consider formation in the water column as a feasible option. We now make this more explicit in the introduction by indicating where the Mn formation is thought to take place with an appropriate reference. We already had included a reference to the carbonate system in the water column where we cited Ulfsbo et al. 2011 (see page 29 line 11).

Modified text (page 4 line 6-15): *"In addition, the formation rate of authigenic Mn minerals in the sediment at deep basin sites may change in response to bottom water hypoxia and anoxia. If release of dissolved $Mn^{2+}$ from Mn oxides - formed at the sediment surface following inflows of oxygenated North Sea water - is the dominant control for Mn carbonate formation in the sediment as suggested for the Gotland Deep (Neumann et al., 2002), expanding bottom water anoxia might allow Mn oxides to be reduced in the water column and at the sediment-water interface, precluding conversion to Mn carbonates. This mechanism was recently invoked to explain the lack of Mn carbonates in the sediment during periods of bottom water euxinia in the Gotland Deep during the Holocene Thermal Maximum (Lenz et al., 2014)."*

11.Molybdenum: The conversion of molybdate to reduced molybdenum species is reasonably complex and depends on the sulfide concentration (Erickson and Helz, 2000; Wang et al., 2009; Wang et al., 2011), so it would be useful to include a line or two on this.

We have now included a comment on the role of the sulfide concentration in determining the accumulation of Mo in the text.

Revised text (page 17 line 18-28): *"Furthermore, these Mn carbonate enrichments occur independently of enrichments in Mo and S. Sedimentary Mo can be used as a proxy for sulfidic conditions close to the sediment-water interface, due to the conversion of seawater oxymolybdate to particle-reactive thiomolybdate in the presence of hydrogen sulfide (Erickson and Helz, 2000). Although the ultimate burial phase of Mo in sulfidic sediments is still debated (e.g., Helz et al., 2011), Mo concentrations have successfully been used to reconstruct the redox history of the bottom water in restricted coastal basins (Adelson et al., 2001; Jilbert and Slomp, 2013a). Sulfur enrichments in sediments are typically associated with Fe-sulfides*

*(Boesen and Postma, 1988), and thus are also indicative of sulfidic conditions close to the sediment-water interface. The independence of Mn enrichments from those of Mo and S suggests relatively oxic conditions at the time of Mn precipitation."*

12. Also it is worth pointing out the strong conservative behavior for Molybdenum in the Baltic (Prange and Kremling, 1985) as due to the low salinities encountered, there are strong vertical gradients in Molybdenum that are not found in other regions. This makes it harder to see small losses of Mo due to scavenging.

Our previous work has shown that Mo is a good proxy for redox conditions in this basin despite the lower salinity (Jilbert and Slomp, 2013a). See revised text in response to point 11.

Specific Comments:
13. P3 Line 30: So how does this mechanism work is it that the pore water Mn2+ is lower as the reduction takes place in the water column?

We have added here that we are referring to conversion to Mn carbonates in the sediments. See revised text in response to point 10.

14. P7 Line 20: Inclusion of the seawater value and error estimates for the flux would be useful to include either here or later in the manuscript as a check to the validity of the flux estimates.

To check the validity of our flux estimates, we compare them to those of other studies (see section 4.1). All data used, including bottom water concentrations are included in Appendix B. We cannot estimate the error for the flux since we have just one porewater profile per site per cruise.

15. P8 Line 18: Is the data on the saturation for FeS included here in the manuscript? As I could not find it listed in the main text.P9 Line 4: It would be useful to also provide here the saturation status for FeS at these sites?

The results of the saturation state calculations for FeS have been included in Appendix B and are now mentioned in the results (page 10 lines 2-4):
*"Pore waters were supersaturated with respect to FeS at the sites in the Northern Gotland Basin (LL19), in the Gotland Deep (BY15) and Fårö Deep (F80) (Appendix B)."*

16. P10 Line 25: In terms of the key processes it would be helpful to state here that release of Mn from sediments with MnO2 present is driven by redox processes, while in the case of MnCO3 it is controlled by the concentration of the solutes and there is no apparent redox change for Mn.

We have made the changes as suggested. Modified text (page 14 line 21-22): *"...release of Mn to the pore water, either from reductive dissolution of Mn oxides or dissolution of Mn carbonates due to undersaturation..."*

17. P11 Line 2: Is there no Mn incorporation into pyrite occurring then?

See reply to point 2 above.

18. P11 Line 26: Is this controlled by the high Mn in the overlying anoxic waters? If so how much of a reservoir effect is this?

We meant to indicate that we were referring to conditions between inflows when the basins are anoxic. We now modified the text to make this clear (page 16 line 28-29): "*Between inflows, when bottom waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are ….*"

19. P11 Line 28: When the oxygenated water comes in to the basin it will obviously take some time to oxidize the bulk of the Mn2+ (Yakushev et al., 2011) and to form that MnO2 that is deposited to the sediment so there is an important kinetic effect here. Also this thin layer of MnO2 is then presumably reduced at the sediment interface resulting in a locally high concentration of Mn2+ which leads to the formation of MnCO3. This all relies on slow diffusion and no resuspension of the Mn porewaters in the sediments.

We have now included that it can take several months to oxidize all the $Mn^{2+}$ and have it settle on the seafloor. We also have added more details on the intermediate role of Mn oxides in the formation of Mn carbonates and have included results of a diagenetic model demonstrating the principle, see responses to comments 5 and 29 of reviewer #4.

20. P14 Line 24: Why does the sulfide return more rapidly? High overlying productivity driving more rapid deoxygenation?

Yes. The eutrophication has led to a higher oxygen demand and the development of anoxic and sulphidic conditions in the water column (Carstensen et al., 2014). We now spell this out explicitly in the text, see response to point 4 of reviewer #4

21. P14 Line 32: I would agree with this as MnO2 in the water column most likely is associated with an organic layer which would reduce its ability to scavenge Molybdate. Most studies that have looked into the ability of MnO2 to scavenge molybdate do not consider the effect of organics (Kashiwabara et al., 2009).

We have deleted this section from the sediment because one of the other reviewers did not agree and it is not key to our paper.

22. P15 Line 24: This sentence needs some qualification as while there might be 8 μM Mn(II) in the bottom waters and shallowest porewaters this might still be insufficient to precipitate out MnCO3 if the carbonate concentration is too low (low pH and/or low alkalinity) (Böttcher, 1997; Böttcher, 1998). There would also

presumably be a sulfide control on the Mn(II) concentration.

We were referring to formation in the sediments following inflows. However, we have now removed this sentence and only refer to this link with inflows at the end of the conclusions section.

23. P15 Line 27: Is the expansion in terms of horizontal area and/or vertical extent? Is there any data that the inventory of Mn in the water column is increasing?

The expansion is in terms of hypoxic area, i.e. horizontal extent, see page 3, line 2 in the previous manuscript and the cited references *("…indicate a major expansion of the hypoxic area in the Baltic Sea").* There is no indication that the inventory in Mn in the water column is increasing over recent decades as we already indicated on page 11, lines 17-18.

We now have modified the conclusions section to include the aspect regarding the hypoxic area. We also more specifically mention the development of bottom water euxinia and the fact that the explanation for the changes in the Mn records we see is a hypothesis.

Modified text (page 22 line 22 and following): "*We hypothesize that this is due to the expansion of the area with hypoxic bottom waters and the development of more continuous bottom water euxinia over the past decades, linked to ongoing eutrophication and possibly due to the reduced input of Fe-oxides that can act as a buffer for sulfides. The high ambient sulfide concentrations in the sediment and water column after an inflow event are suggested to contribute to conditions that are conducive to a faster dissolution of Mn oxides, leading to less formation of Mn carbonates and more loss of $Mn^{2+}$ to the water column. Our hypothesis is supported by the results of a simple diagenetic model for Mn. It is also in accordance 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). In the Landsort Deep, in contrast, Mn sulfides and carbonates are still being precipitated. This could be due to strong focusing of Mn rich sediment particles and high rates of sediment accumulation in the Landsort Deep. Our results indicate that sediment Mn carbonates in the other deep basins of the Baltic Sea no longer reliably and consistently record inflows of oxygenated North Sea water.*"

24. Table 2: It would be helpful here to also include the Mn(II) concentration in both the overlying water and at the top of the porewater profile to show that the flux is real. In this context if a dissolved Mn inventory for the anoxic waters was constructed it would allow a turnover time for this pool to be estimated using the fluxes listed here. This would help to answer the question of how long it takes to resupply the bottom waters after an oxygenation event.

The requested data were already included in Appendix B. We now have added a reference to the appendix in the caption of Table 2. We also have added an inventory for dissolved $Mn^{2+}$ in the text and compare it to the benthic flux. The benthic fluxes directly after an inflow are expected to be higher than current fluxes. This is now indicated in the text where we cite the work of Neretin et al. (2003). For further details, see response 18 to reviewer #4.

## Response to reviewer #3 (minor revisions, on 1. revised version)

The manuscript by Lenz and colleagues provides new insight into the cycling and sequestration of Mn in the water column and sediments of the Baltic Sea euxinic basins, linked to recent changes in the extent of hypoxia. Their analytical results and scientific interpretations are interesting and are suited for publication in Biogeosciences. Furthermore the comments from both reviewers and subsequent revisions by the authors have significantly improved the manuscript. Nonetheless, several minor and some major points remain that, in my opinion, need to be revised before the manuscript can be accepted for publication. Page and line numbers refer to the revised manuscript version.

Minor comments:

1. Add to introduction:
Matthäus, W., Franck, H., 1992. Characteristics of major Baltic inflows — a statistical analysis. Continental Shelf Research 12, 1375–1400.
and/or

Matthäus, W., Nehring, D., Feistel, R., Nausch, G., Mohrholz, V., Lass, H.U., 2008. The inflow of highly saline water into the Baltic Sea. In: Feistel, R., Nausch, G., Wasmund, N. (Eds.), State and Evolution of the Baltic Sea, 1952–2005. A Detailed 50-year Survey of Meteorology and Climate, Physics, Chemistry, Biology, and Marine Environment. John Wiley & Sons, Hoboken, pp. 265–309.

References now added in the introduction where we first mention the Baltic inflows (page 3, line 13, after *"deep basins").*

2. Page 3, lines 26-30: In both sentences it is not clear what is happening in the water column vs. the sediment. I suggest adding "in the sediment" where appropriate.

We modified these lines to include more specifically where each process is likely taking place, see response to point 10, reviewer #5.

3. -Page 5, line 3: Is the bottom water sample taken from the water overlying the multicore ? Please mention.

We added a sentence to clarify this. Revised text (page 5 line 19-20*): "A bottom water sample was taken from the water overlying the sediment in each multicore as soon as possible after core collection".*

4. -Page 5, line 10: Spell out ICP-OES when used the first time.

We now write ICP-OES (page 6 line 1) as *"Inductively Coupled Plasma – Optical Emission Spectroscopy"*

5. -Page 5, line 27: Based on the analyses of laboratory reference materials and replicates, the relative error of the organic C measurement was generally less than 5%.

We have rephrased this sentence as suggested by the reviewer.

6. What are the detection limits for the ICP-OES analyses ?

We added the detection limits for the ICP-OES for all relevant elements in solution in the text (page 7 line 8).

7. Page 8, line 28: Please find a more scientific term than "hand in hand".

We rephrased *"with the increase going hand in hand with a decline"* to *"simultaneously with a decline" (page 11 line 26).*

8. -Page 10, line 19: It would be helpful to provide at least some evidence that the eastern Gotland Basin sites (LF1 and LF3) ever did act as significant sources of Mn to the water column. In this section Lenz et al. suggest that, since these two sites are devoid of Mn both in the pore-water and in the solid-phase (in the top 45 cm of the sediment sampled in this study), they "no longer do so". This implies that they previously were characterized by significant Mn fluxes to the water column, and accordingly higher Mn solid phase values. I suggest at least adding a reference to Lepland and Stevens (1998) or any other study that provides some support for this hypothesis and a sentence discussing this. If the authors want to assume that all sites in this study receive(d) the same terrestrial Mn input over time they need to state this.

Given that - to our knowledge - there are no previous studies on Mn for the same area we cannot refer to such a paper (note that the Lepland and Stevens (1998) paper does not include data for this geographical area). We have modified the text to remove the suggestion that these areas likely previously were sources of Mn but we do mention the likely transient nature of the source because of the low solid phase Mn contents in the sediment.

Modified text (page 14 line 13-15): *"At one of the sites on the slope of the eastern Gotland Basin (LF1) there is also a significant release of $Mn^{2+}$ but the sediments at this* *site are low in Mn in the solid phase. This suggests that the source of Mn at this site may be of a transient nature."*

9. -Page 10, lines 28-29: "Diffusive fluxes" occur everywhere (i.e. also within the sediment). The authors need to specify that they refer to a diffusive flux of Mn into the water column here.

Comment on revised text. We followed the recommendation of the reviewer and now write (page 14 line 23-24): *"diffusive Mn fluxes from the sediment to the water column"*

10. -Page 12, lines 1-5: The authors have changed this section compared to the original manuscript, taking out their hypothesis that high alkalinity contributes to Mn carbonate formation in the deep basin. However, as it is written now, it is unclear what they want to say with "high alkalinity in sulfate-bearing organic rich sediments overlain by an anoxic water column are typically linked to organic matter degradation through sulfate reduction (Berner et al., 1970)", since alkalinity is not mentioned previously. I suggest revising this section using part of the old sentence and the revised sentence.

Comment on revised text. We followed the suggestion of the reviewer and now combine the old and new text. Text added (page 17 line 8-11): *"We suggest that this water depth effect between the deep basin sites is due to increased focusing of particulate Mn oxides precipitated during inflow events with water depth, combined with a high alkalinity in the deep basins linked to organic matter degradation by sulfate reduction".*

11. -Page 13, line 27: What does "their occurrence" refer to ? Reducing conditions ? Inflow ?

Comment on revised text. We now repeat the word inflow and changed the sentence to (page 19 line 16-17): *"Given the suggested link between Mn burial and inflows, it is important to assess the occurrence of these inflows"*

12. -Page 13, lines 14-22: This section lacks an explanation on what the low Mo concentrations and the correlation of Mn enrichments with these low concentrations mean. I suggest adding a sentence after "At site LL19,.." and "At LD1,…" stating e.g., " This suggests that…" or "This supports our hypothesis that".

We rephrased the text as suggested by the reviewer.

Revised text (page 19 line 5-12)*: "At site LL19, Mn enrichments in the sediments coincide with low values of Mo in the sediment and inflows of oxygenated water. This suggests that Mn burial is enhanced under more oxygenated bottom water conditions. At LD1, in contrast, high Mn contents are observed from 1965 onwards, independent of inflows, with the highest Mn values coinciding with periods with the highest sulfide* *concentrations that occur in particular since the year 2000. 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 the other basins."*

13. Page 13, line 24: Again, before using Mo records to imply "more reducing conditions" the authors have to at least once state the biogeochemical background for that, including references etc.

We included a section in lines 18-23 on page 17 explaining the use of Mo as a proxy for the presence of hydrogen sulfide in the bottom water. See response to point 11, reviewer #5.

14. Figure 2: I suggest plotting the pore-water Mn concentration of LD1 on a different scale than the other sites, i.e., plot the data for the other sites on a 0-300 uM scale. The authors have done that for the solid-phase Mn data and it makes it much easier to read the plot.

We have changed the scales in Figure 2 as suggested.

Major comments:

15. -Page 7, line 18 and below: The Mn flux calculation for Site LF 3 is misleading. The authors did not measure the bottom water value during their 2011 cruise but note a value of 11 µM for the sample from 1 cm sediment depth. Given that the bottom water likely has a value of around 1 µM, this suggests that there was a flux of Mn out of the sediment. For their calculation, however, they use data from their 2009 cruise where they essentially measured the same value for the bottom water and the 1 cm –sample. It is unclear why the 2009 value for the 1 cm-sample is so much lower than the 2011 value, and may indicate problems during the MUC sampling (i.e., disturbance of the surface fluffy layer). However, to report a flux of 0 and to ignore the 2011 data to me is not the right approach; especially since most of the flux calculations for the other sites are based on the 2011 values. I suggest excluding the calculated value of 0 from the table and discussion.

We had no indications for any disturbance of the surface fluff layer during sampling in 2009 or 2011. We note that LF3 was located only slightly below the chemocline at the time of sampling. The chemocline in this area displays strong vertical variations in water column concentrations of $Mn^{2+}$ with values ranging from 1 to 15 µM (e.g. Dellwig et al., 2010). We therefore would not dare to speculate about the bottom water concentration of $Mn^{2+}$ in 2011.

To avoid confusion, we have followed the suggestion of the reviewer and have removed site LF3 from Table 2 and the corresponding text.

16. -Page 8, line 20: Carman and Rahm (1997) use (asides from H2S etc.) the concentration of phosphorus to calculate carbonate alkalinity from titration

alkalinity and even note that it is an important contributor. Lenz et al., however, do not show phosphorus data and it is not clear whether they included phosphorus in their calculation. If not, then their statement "Carbonate alkalinity was calculated from titration alkalinity as described by Carman and Rahm (1997)." is incorrect, and they need to state how they exactly determined carbonate alkalinity.

As indicated in the text, we followed the calculation of Carman and Rahm (1997). Thus, we included phosphate porewater data in our calculations. Most of those data have been published previously (Mort et al., 2010, Jilbert et al., 2011, Jilbert and Slomp, 2013b). We have now also included these phosphate data in Appendix B.

17. -Page 12, lines 27-30: That's a big, non-intuitive step going from sediment deposition rates to pore-water profiles. The authors need to do a better job elucidating the mechanistic connections here, e.g., high deposition rates  high TOC and Mn solid accumulation rates  higher organic carbon mineralization rates …or whatever their train of thought is. These links are not straightforward and need to be better explained to the reader, even adding some references.

We provide more details on the possible mechanisms in the revised text as detailed below.

Revised text (page 18 line 4-17): *"However, the pore water $Mn^{2+}$ concentrations at Landsort Deep site are much higher than elsewhere (> 1 µM versus <0.26 mM of $Mn^{2+}$). This may be related to the fact that the Landsort Deep is the deepest basin in the Baltic Sea and its geometry makes it an excellent sediment trap. As a consequence, sediment deposition rates are much higher than in the other Deeps (Lepland and Stevens, 1998; Mort et al., 2010). Results of the recent IODP expedition suggest that deposition rates may even be more than a factor of 6 higher (Expedition 347 Scientists, 2014). Sediment focusing is also expected to lead to a higher input of Mn oxides to this basin. Given that rates of mineral dissolution are expected to depend on the amount of material present, corresponding rates of input and dissolution of Mn oxide minerals in the sediment are likely higher in the Landsort Deep than at other sites. Thus, we suggest that differences in focusing of the sediment may explain the observed differences in pore water chemistry and Mn sequestration. The differences in pore water chemistry will also likely impact the exact solid phases formed in the sediments of the various deep basins."*

18. -page 14, lines 27-33: This is the weakest section of the manuscript discussion and I agree with Reviewer#2 that it is highly underdeveloped and needs revision. In fact, I am surprised that Lenz et al. have ignored the very valid suggestions the reviewer makes and instead decided to only minimally rephrase this paragraph. The biogeochemical cycling of Mo under different oxygen levels/redox conditions is a highly debated field with many important implications for early Earth environments. Thus, the authors are not doing themselves a favor by including such a superficial discussion section in their manuscript. Reviewer#2 is correct in pointing out that the authors do not correctly interpret the

observations/publication by Scholz et al. (2013). Indeed, Scholz et al. (2013) suggest that: “Our data reveal that multiple mechanisms are likely contributing to Mo burial, including scavenging of thiomolybdate (or other Mo-sulfide-complexes) or Fe–Mo–S nanoparticles by organic matter during euxinic periods and adsorption of molybdate by Mn and Fe (oxyhydr)oxides during more oxic periods.” This is actually not contradicting what Lenz et al. observe. At the same time the reviewer even gives Lenz et al. a guideline of what to discuss, including the different transport pathways for Mo, the Mo shuttle mechanism, and the differing mobility/diagenetic behavior of Mn and Mo under anoxic-sulfidic conditions. If the authors wish to simply “suggest that the Mn shuttle is not the main carrier for Mo to the sediment”, I also suggest proposing an alternative mechanism and to highlight the differences of their model to that of Scholz et al. (2013). As pointed out by Reviewer #2 the data from Lenz et al., predominately indicate that Mn oxides are not the main burial phase for Mo. I suggest discussing the correlation between TOC and Mo concentration they observe, which points to Mo bound to organic matter as a primary burial phase. In this context Scholz et al. (2013) state: “In agreement with sediments from many other euxinic basins (Algeo and Lyons, 2006), however, Mo concentrations are well correlated with TOC..[..]. As a result, TOC concentrations are highest adjacent to the rhodochrosite layers. Much of the Mo bound to organic matter might have been scavenged as thiomolybdate in the water column during euxinic periods (Nägler et al., 2011). However, given the high Mo and H2S concentrations in the porewater, ongoing sequestration of Mo by organic matter is likely to occur after deposition and during burial. We therefore assume that a significant portion of the Mo delivered by Mn and Fe (oxyhydr)oxides is ultimately buried in association with organic matter.” I suggest to at least consider this aspect.

Our paper centers around Mn dynamics, not Mo dynamics. We included the lines on Mo because the water column data clearly indicate that the Gotland basin has been permanently euxinic over the past decade and that <u>at present</u> Mn oxides thus cannot act as a carrier of Mo to the sediment – this differs from the interpretation of the <u>present-day</u> Mo profiles for the Gotland basin in the paper of Scholz et al. (2013) where Mn shuttling is suggested to be an active process. This is what we wrote in the text and did our best to clarify in our response to reviewer #2. Note that reviewer #5 agrees with our interpretation.

Given that our paper focuses on Mn, we find that a detailed discussion of Mo geochemistry including the various burial phases of Mo and the relationship with TOC as now suggested by reviewer #3 lies outside the scope of this paper. As indicated in our previous response, some of us have recently published two other papers discussing the relationship between Mo and TOC in Baltic Sea sediments in Geology (Jilbert and Slomp, 2013a and 2015).

We now followed the alternative suggestion of reviewer #2 in the previous review round (see below) and removed this section from the paper.

19. -page 15, lines 15-20: As already pointed out by Reviewer#2, the results from Landsort Deep are indicative of the present "transitional phase" of this environment. The enrichment of Mn under anoxic conditions only works because of the deep Mn source accumulated under oxic conditions. I agree with Reviewer#2 that it makes more sense develop an "indicator for the transitional state between intermittent and permanent anoxia", which would add to the value of the manuscript, rather than to only state that multiple redox proxies should be applied.

We have removed the section on the deep sediment source of $Mn^{2+}$, thus this comment is no longer relevant.

## Response to reviewer #1 (rejection, on 1. revised version)

**modified response in orange**

Substantial items of the original comments were not addressed and I am not convinced that hypoxia will lead to enhanced reductive dissolution rates for Mn oxides.

We regret that the reviewer did not provide further details on the items he/she did not find to be addressed. We have now expanded our answers even further, have made additional modifications in the text and have added results of a simple diagenetic Mn model demonstrating that an increase in Mn oxide dissolution kinetics (within a range that is possible for the Baltic Sea) could explain the lack of Mn carbonate formation. We thus demonstrate that the higher sulfide concentrations could play a key role in decreasing the time available for the conversion/transformation of Mn oxides into Mn carbonates by enhancing the rate at which the Mn oxides are reduced by sulfide, simply because sulfide is so much more abundant than before. Rates of reduction of Mn oxides by sulfide are known to depend on the concentration of sulfide (e.g Wang and Van Cappellen, 1996; equation II-9, page 2998), so this is a plausible mechanism. This is now included in the text in sections 2.7, 3 and 4.3.

Note that this explanation is not questioned by reviewers 2, 3 and 4 and in fact forms the basis of the use of Mn as a paleo-redox proxy, where absence of Mn carbonates in sediments is assumed to be indicative of euxinic (i.e. anoxic and sulfidic) bottomwaters for over two decades (e.g. Calvert and Pedersen, 1993) as confirmed by reviewer #4.

We cannot prove that it is the expansion of the hypoxia that is driving the lack of Mn carbonate formation in recent sediments. That is why we included a question mark in our title. We have now modified the text in the abstract, discussion and conclusions to make clearer that our suggested explanation that increased sulfide concentrations in the bottom water and sediment play a role is a hypothesis. We also more specifically refer to the evidence for similar processes from the geological record.

## Response to reviewer #1 (rejection, on first version)

**modified response in orange**

We thank the reviewer for the comments on our manuscript and provide detailed answers to each point raised below. Line numbers refer to the original manuscript.

1: The authors generally consider the formation of pure MnCO3, rhodochrosite, in the text and their thermodynamic calculations, although it is known, that the authigenic phases formed actuyll consist of CaMn carbonate solid-solutions with a wide range of compositions and thermodynamic properties (Suess, 1979; Jakobsen & Postma, 1989; Böttcher & Dietzel, 2010).

We do not assume the formation of pure $MnCO_3$. We refer the reviewer to page 9891, line 3-6 where we write: ”*In anoxic settings, Mn enrichments are typically assumed to consist of Mn carbonates, which are often associated with calcium and can contain other impurities (e.g. Jakobsen and Postma, 1989, Manheim , 1961, Sternbeck and Sohlenius, 1997, Suess , 1979*)”.

Given the lack of data on thermodynamic properties of the Mn carbonates minerals in these sediments, we followed the approach used in earlier studies (e.g. Carman and Rahm, 1997). But to improve our results, we now have replaced the calculation of the saturation index (SI) for rhodochrosite and calcite by that for the $Mn_{0.74}Ca_{0.26}CO_3$ solid solution according to Katsikopoulos et al. 2009. Still given the broad variability of $MnCO_3$ contents in the solid solution and our lack of knowledge of other constituents, the results only give an indication of the possibility to form certain Mn bearing carbonates.
We have changed the corresponding sections in the paper. This means we changed Figure 3 and the methods section in (2.6 Saturation state, page 9897 line 13):

“*Thermodynamic equilibrium calculations were performed for the pore waters of LF3, LL19, BY15, F80 and LD1 using version 3.1.1 of the computer program PHREEQC (Parkhurst and Appelo, 1999) with the LLNL database. The data base does not contain the authigenic carbonate phase present in the Baltic Sea. Data from the literature (Jakobsen and Postma, 1989; Sternbeck and Sohlenius, 1997; Lepland and Stevens, 1998; Huckriede and Meischner 1996; Kulik et al., 2000) suggests that carbonates mainly consist of Mn and Ca. Therefore, an approximation of the solubility product of (Mn, Ca)* $CO_3$ *solid solutions was generated using the equations given in Katsikopoulos et al. 2009. The stoichiometric solubility product (Kst) was calculated using* $Mn_{0.74}Ca_{0.26}CO_3$ *(Kulik et al 2000) as a common ratio measured for (Mn, Ca)*$CO_3$ *solid solutions in Baltic Sea sediments.*

*An equilibrium constant pK of 0.377 (Emerson et al. 1983) was used for Mn sulphide. The solubility of iron sulfide from Rickard (2006) was added to the calculations as well as $MnHS^+$ as a solute (Luther et al., 1996) because it is likely abundant in pore water in sulfidic sediments (Heiser et al., 2001). Carbonate alkalinity was calculated from titration alkalinity as described by Carman and Rahm (1997)."*

We now also have added additional text in the introduction explaining that when we mention Mn carbonates, we are aware that the actual minerals are more complex:

Page 2, lines 18-20*: "For simplicity, in this study these phases are collectively referred to as Mn carbonates, despite their obvious greater complexity and heterogeneity."*

We have also added additional text in the methods to explain the goal of our calculations (page 9 line 11-14):

*"Our calculations should be seen as approximations only with the main purpose of providing a comparison to previous calculations by Carman and Rahm (1997) and Heiser et al. (2001) to assess whether there are any indications for a change in saturation state of the porewater between inflows."*

We also have added the following text in the discussion to make clear that the saturation state calculations are of relatively limited value (page 16 line 28 and following):

*"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)."*

2. Most details facing analytical instruments, sensors, standards used, analytical precision etc. are missing in the Material & Methods part.

We have added more specifications of the instruments and the analytical precisions (see method section 2) . We now also refer to various previous papers describing the sediment and porewater sampling at these stations in detail and we have expanded the methods section (also see reply to reviewer #3):

*3. -9890-6 and 09893-7: 'well dated sediment cores'. Looking on the raw data presented in the appendix for two investigated sites of this study there are some unusual trends (maxima) observed in the 210Pb profile, that question the term 'well-dated'. Unfortunately these results are not discussed in detail in the manuscript.*

The age model for one of the two sites mentioned above (BY 15) was published by Jilbert and Slomp (2013b) and is discussed in detail in the supplement of that paper. We have therefore removed the description of the age model for BY15 from our paper and refer to the relevant published work. However, we have included a brief discussion of the age models for LD1 and F80 in an appendix to the current submission.

We note that deviations of $^{210}$Pb profiles from an exponential decline with depth are not unusual in Baltic Sea sediments and are likely the result of variations in sedimentation rate, due to non-constant lateral and vertical sediment fluxes. Usually, such deviations are small and do not change the overall trend of the $^{210}$Pb profile, as is the case for BY15 (Jilbert and Slomp, 2013b). For LD1, the $^{210}$Pb deviations are larger, possibly due to the high and variable concentrations of authigenic minerals (see Micro XRF maps in Figure 5) which dilute the mass-normalized $^{210}$Pb activity. These factors make LD1 the least well-dated of all cores in this study. However, the uncertainty in the age model of LD1 does not affect our conclusions and the results are in line with a previously published sediment record for Mn for the Landsort Deep (Mort et al., 2010). Because of the relatively higher uncertainty in the dating of LD1, we now write "*dated cores*" instead of "*well-dated*" cores in the abstract and text, where relevant.

Continued work on the sediment geochemistry for site F80 in our lab recently revealed that the previously published age model for F80 could be improved, using LA-ICP-MS profiles of Mo and Mn, and coupling these to known events in the oxygen history of the Fårö Deep. We now present this revised age model in the supplementary information file and use that revised age model in the paper.

4. -9890-20: -Why should hypoxia increase the reaction rate between hydrogen sulfide and Mn-oxide? This is always a very fast reaction that will take place in top sediments as soon as sulfate reduction starts.

Here, we wish to explain our observation that Mn carbonates no longer form after inflow events. We hypothesize that this is due to the much quicker return of sulfide and higher concentrations in the bottom water and surface sediments after an inflow event. This is likely due to the faster rates of sulfate reduction than in the past linked to the ongoing eutrophication of the system and the lower input of reactive Fe, as reflected in the Fe/Al ratios, with less Fe thus buffering the sulfide formed in the sediment. The Mn oxides are thus more quickly exposed to high sulfide concentrations after an inflow and as a consequence, may be lost before Mn carbonates can form. Furthermore, since of rate of reduction of Mn oxides by sulfide depends linearly on the concentration of sulfide (Wang and Van Cappellen, 1996), hypoxia will indeed increase the reaction rate between $H_2S$ and Mn oxide. We now have included the results of a diagenetic model for Mn demonstrating that this is a possible scenario.

*We added (start: page 21 line 1): "We hypothesize that Mn oxides that are formed following modern inflow events and that are deposited on the seafloor (Heiser et al., 2001) are no longer being converted to Mn carbonates because of higher ambient concentrations of sulfide in the bottom water and in the pore water. These higher* *sulfide concentrations are likely the direct result of increased sulfate reduction driven by the ongoing rise in productivity in the Baltic Sea (Gustafsson et al., 2012). The observed decline in Fe/Al at our deep basin sites (Figure 3) suggests more muted shuttling of Fe oxides from shelves to the deeps linked to the expanding hypoxia (e.g. Scholz et al., 2014) which may have reduced the buffer capacity of the sediments for sulfide (e.g. Diaz and Rosenberg, 2008).*

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

$$R = kC_{TS}C_{Mnoxides} \qquad (6)$$

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

$$R = k_{red}C_{Mnoxides} \qquad (7)$$

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

5. -9891-14: The authors state that the formation of MnCO3 and MnS is driven by 'exceptionally high alkalinity'. This is not completely correct. Pore water alkalinity consists mainly of dissolved carbonate (DIC) thereby promoting the formation of the Mn(II) bearing carbonate but preventing the formation of MnS. Since sulfate reduction is the main process responsable for alkalinity generation in the sediments of the Baltic Sea deeps, there is twice as much of CO2 produced compared to hydrogen sulfide.

In the introduction, we are directly citing the paper of Lepland and Stevens (1998) who in their paper state that high alkalinity is important for the formation of both Mn carbonates and Mn sulfides. Note that in our data for station LD1 (especially the XRF maps, fig. 5), MnS and Mn carbonates are present in layers that overlap suggesting a similar environment of formation.

However, we have modified the statement as suggested by the reviewer to avoid confusion and now write (page 2 line 27-29):

*"The formation of Mn carbonate is assumed to be driven by an exceptionally high alkalinity. Mn sulfides form when $H_2S$ exceeds Fe availability (Böttcher and Huckriede, 1997; Lepland and Stevens, 1998)."*

6. -9895-25: How did the authors prevent sediment distrubance upon the use of cores with such a small diameter? Why did they observe a loss of 50% during the replacement of water by the Spurr method? Normally, the water volume deficit should be compensated by the resin. –

The XRF-maps show intact laminations, which is an indication that no major disturbance occurred during sampling. The application of the Spurr´s resin method to surface sediments, as done here, is not directly comparable to that of deeper sediments because of the much higher water content of the former. This explains the greater loss of length that occurs during the dehydration step when the water is replaced with acetone, which has a far lower surface tension. This step has to be repeated several times and takes up to 10 days in which the sediment sub-cores stand upright. This is explained in the methods section (9896 lines 1-5) and in the paper where this method was first applied to surface sediments (Jilbert and Slomp, 2013b).

7. -9897-14: The authors follow the approach already used by Carman & Rahn giving essentially the same results as published in 1997. The question remains, why pure MnCO3 and CaCO3 were used: Solid-solutions are the actual phases with solubility products deviating from ideal mixtures (see above).

See answer to comment 1 above.

8. What is the actual mineralogy considered by Emerson et al.(1983) for MnS?

The MnS phase described in Emerson et al. (1983) is Alabandite. While γ-MnS may be the actual phase forming in the Baltic Sea, no thermodynamic data for this phase have been published. The equilibrium constant from Emerson et al. (1983) gives reasonable results that are in accordance with our solid phase results that show formation of MnS.

9. The authigenic phases observed in the Baltic Sea are unusual and different MnS modifications will have their distinct thermodynamic stabilities. The authors refer to Heiser et al. (2001) to justify that the ion pair $MnHS^+$ may have to be considered in the thermodynamic evaluation of the pore waters. But how can the reported field study from the Baltic prove this?

We do not wish to prove this and we do not state that we prove this in the paper. We are using this knowledge in our calculations given that the presence of this mineral has been suggested and we are focusing on the Mn carbonates and are including the MnS for completeness. The section on the saturation state calculations is of relatively minor importance in our paper and its only purpose is to check whether conditions between inflows are still the same as in the past, i.e. whether our results are similar to those of previous studies several decades ago. This is now explained in further detail in the text.

10. -9898-10: The saturation states of the pore waters are in particular controlled by the pH of the solutions (not shown in the ms). In the present study these have been measured in filtered pore waters after extensive centrifugation (up to 30 min). This allows significant dgeassing of CO2 (and if present H2S) leading to a shift in pH towards higher values thereby enhancing the saturation degrees wrt. carbonate and sulfide minerals. Instead of discussing other effects like phosphate availability (9904-13) the authors should discuss the potential impact the sampling procedure had on their analytical results.

We have added all the pore water and sediment data including the pH values in the supplement of the manuscript. We have no indication for major effects of the length of the centrifugation time on the pH or sulfide values. Note that most sediments were centrifuged much shorter than 30 minutes, which was only the maximum time used in cases with particularly stiff sediment (e.g. the deeper sediment at LF3). Note also that our sulfide concentrations are similar (or higher) and that pH values are within a similar range to those reported for Baltic Sea sediments in other studies (e.g. Carman and Rahm, 1997). However, we are aware that degassing always impacts ex-situ pH measurements, regardless of the method of pore water collection used. Note also that an upward shift of e.g. 0.5 pH unit would not affect the observed trends and contrasts with depth and between stations in the saturation state calculations. Also, the saturation state calculations are not critical to the main message of the paper and are not critical to our conclusions, see above.

This is now mentioned in the methods (page 5 line 8-10):
*"Note that degassing of $CO_2$ may impact ex-situ pH measurements and may lead to a rise in pH (Cai and Reimers, 1993). As a consequence, our pH values should be seen as approximations only."*

And (page 12, line 4-8):
*"Note that degassing of $CO_2$ during centrifugation may have led to a shift in pH to higher values, thereby enhancing the degree saturation with respect to carbonate and sulfide minerals. However, an upward shift of ca. 0.5 pH units due to this effect would not greatly affect the observed trends with depth and contrasts between stations in the calculated saturation states presented."*

We have also added additional text in the methods to explain the goal of our calculations and their limited value (see response to reviewer #4)(page 9 line 11-14):

*"Our calculations should be seen as approximations only with the main purpose of providing a comparison to previous calculations by Carman and Rahm (1997) and*

*Heiser et al. (2001) to assess whether there are any indications for a change in saturation state of the porewater between inflows."*

11. -9900-18: Are these really Fe(III)-phosphates or actually FeOOH with adsorbed phosphate?

Dellwig et al. (2010) write: "*Most of the analyzed particles are star-shaped, of about 5 micrometer in size, and occur as single particles or aggregates without any morphological differences between Mn oxides, Fe-oxyhydroxo-phosphates, and mixed phases. Throughout the redoxcline, these minerals show a general succession with maximum abundance of Mn oxides above the redoxcline followed by mixed phases and almost pure Fe-phosphates within and below the redoxcline, respectively*". Further in the manuscript, they write that the Mn-Fe-phosphates are formed through: "*stepwise replacement of Mn(IV) by Fe(III) on sinking $MnO_x$ particles followed by immediate adsorption or even co-precipitation of phosphate*". Thus, 'Fe(III) phosphates' refers to both precipitates of Fe-(III)-P and sorbed P on Fe-oxides.

For clarity, we have changed the term in the manuscript to "*mixed phases of Mn oxides and Fe-(III)-associated phosphates*". Note that this is not relevant to our discussion, which concentrates on Mn, not Fe and phosphate.

12. -9901-5: Why 'now'? Isn't this the general case for the Baltic deeps?

Here, we are referring to the contrast to the initial expansion (described in the previous sentence) when coming from an oxic, nearly Mn free water column. Dissolved Mn enriches in the newly anoxic water column. The water column now rather contains a more or less constant pool of Mn (as confirmed by the water column data of Pohl and Hennings 2005 and Turnewitsch et al. 2010) with no major additional inputs. Only changes in redox conditions "*temporarily*" change the Mn concentration.

We have now removed this sentence.

13. -9901-16: The increase of supersaturation in MnCO3 after inflow events was not shown by Meischner & Huckriede (1996), only assumed.

We agree with the reviewer. That is why we wrote: "*strong oversaturation may be reached*".

To clarify this point further, we now write (page 17 line 1-5): *"The dissolution of Mn oxides in the surface sediment following an inflow of oxygenated North Sea water is thought to lead to high $Mn^{2+}$ concentrations in the porewater 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)*

14. -9901-25: reference?

Here the reviewer refers to the sentence: "*We postulate that this water-depth effect between the deep basin sites is likely due to increased focusing of particulate Mn oxides precipitated during inflow events with water depth, combined with a high alkalinity linked to organic matter degradation by sulfate reduction*".

We have changed the word "*postulation*" to "*hypothesis*" throughout the manuscript for clarity. We also now supply references supporting the suggested mechanism: "*Increased focusing of Mn oxides with water depth has been observed in other marine systems (e.g. Slomp et al., 1997) and high alkalinity in sulfate-bearing organic rich sediments overlain by an anoxic water column are typically linked to organic matter degradation through sulfate reduction (Berner et al., 1970).*"

15. -9902-25: How can more reducing conditions yield MnS formation? The pore waters of the LD are mostly sulfidic, in contrast to the euxinic water column. There will be no impact of external boundary conditions on the MnS formation. Textures and geochemistry of these minerals demonstrate that they often are formed under slow precipitation conditions in the sediment. And: More rdducing conditions (means more sulfide?) should also rise the DIC level, thereby promoting MnCO3 instead of MnS precipitation.

We observe increased formation of MnS and wish to provide a possible explanation for that observation. We did not investigate the texture and further geochemistry of the minerals formed in the surface sediment at our site. We simply speculate about the possible causes for the observed MnS formation and observe a correlation with Br and Mo in our data that suggests a possible mechanistic link with the input of organic material and higher sulfide concentrations in the porewaters. Of course, the decomposition of organic material would also raise the DIC level but again our data shows the formation of MnS in close proximity to the $MnCO_3$ and there is no indication of a change of environmental conditions between the formation of the two minerals in the sediments.

We have now modified the text on page 9903 to indicate better that these are speculations: Line 1: changed to "*possibly suggesting rapid changes in Mn mineralogy in response to seasonal variability of the organic matter flux (Fig. 5). [....] Further work is required to determine conclusively what the mechanism of formation is of the MnS.*"

16. -9904-17: As written correctly, this is a postulate, but what is the actual base for this? Why should Mn oxides be reduced faster without enhancing the rate of MnCO3 precipitation? The reacion rate of H2S von MnO2 is very high and an increase in alkalinity will also lead to an enhanced MnCO3 precipitation rate.

We refer to our answer to a similar comment above. Our postulation is based on the observation that there are less Mn carbonates in the sediment at all sites (except LD1) compared to several decades ago. This observation is in line with trends in burial of Mn during previous periods of hypoxia in the Baltic Sea as observed at site

LL19. We wish to provide a possible mechanism for this change. Given the greater abundance of sulfide in the bottom waters of the Baltic Sea over the past decades (see Figure 7), and the accumulation of Mo in the surface sediment, which is an indicator for sulfide in porewaters, we hypothesize that Mn oxides no longer survive long enough to allow for efficient retention of the $Mn^{2+}$ as Mn carbonate, as is observed in other euxinic basins (Calvert and Pedersen, 1996).

We have modified the text to make more clear that this is a hypothesis and how the high sulfide may be linked to eutrophication and decreased Fe inputs (response to reviewer #4 comment 4). In response to reviewer #4, we also discuss other possible reductants for Mn oxides and include results of a diagenetic Mn model demonstrating the feasibility of the suggested mechanism. For further details, see the relevant responses above.

17. -9904-23: Here it would be appropriate to refer to Neubert et al. (2008, Geology) and Nägler et al. (2011, Chem Geol).

This section has been removed from the manuscript.

18. -9914-Fig.2: Why are the dissolved sulfide data called 'HS-'? Although this is the dominant species at the expected pH, there will be some H2S(aq), that was measured together with bisulfide in the pore water.

We agree with the reviewer that some $H_2S$ will be present as well. We have now added a statement in the caption of the figure that "*while dissolved sulfide is here expressed as $HS^-$, some $H_2S$ is present as well*".

19. Looking on the pore water of station LD1, two things are unclear to me: First the sulfate profile looks rather unusual: A complete depletion of sulfate in the top cm of a short sediment core is normally not observed in the deeper parts of the Landsort deep. Could it be that some sediment loss took place during sampling?

To our knowledge, there is only one pore water profile of sulfate for surface sediments in Landsort Deep in the published literature (Mort et al., 2010; GCA – included in their supplementary information). While indeed the decline in sulfate at the sediment water interface is much sharper here, the sedimentation rate at this site and the concentrations of other pore water species (e.g. $NH_4^+$) are also higher. This suggests a much higher rate of organic matter degradation at this location than the one in Mort et al., 2010. We have no indication for loss of surface sediment during sampling, and the porewater profiles for other constituents (e.g $NH_4^+$, Alk) show the expected shape. The spatial variability in sediment characteristics in the deep basins of the Baltic Sea is known to be very high. Further work is needed to assess the range of sulfate gradients in the pore water in the Landsort Deep.

20. Second: It is stated in the methods part that the Mn fluxes were estimated from the gradient thorugh the top 0.5 cm of the sediment. For station LT1, the first data

point available is from about 2.5 cmbsf and no bottom water value seems to exist. So, the question remains which data were used to estimate the gradient to derive the flux? The same question comes up for station Fladen BS1: This is a site with oxic bottom water, but the calculated flux given in Table 2 is relatively high. A look on the details of the dissolved Mn2+ profile, however, shows that looking vertically upward Mn already goes down to zero below the sediment-water interface. So no flux out of the sediment would be expected.

Although a bottom water sample was taken at LD1, it was inadvertently not processed for all analyses and thus indeed no data for $Mn^{2+}$ are available. As an approximation, we assumed a $Mn^{2+}$ concentration similar to the one published for the Landsort Deep by Mort et al., 2010 of 3.1 µM. This is now described in the text and in the caption of the Table. At site BS1, the $Mn^{2+}$ flux was based on the difference in concentration between the bottom water concentration of $Mn^{2+}$ (2.5 uM) and the first measurement at 0.75 cm depth (22.9 µM). Indeed, the $Mn^{2+}$ flux is relatively high for an oxic site. Because of the relatively coarse depth resolution of the profile, removal of $Mn^{2+}$ between 0.75 cm and the sediment-water interface is expected. We have now removed the flux calculation for this site from the manuscript.

## Response to reviewer #2 (minor revisions, on first version)

**modified response in orange**
Page and line numbers refer to originally submitted manuscript

We thank the reviewer for the comments on our manuscript and provide detailed answers to each point raised below. Line numbers refer to the original manuscript.

1. Page 9902, after Line 8: The authors claim that the high deep-sourced Mn flux (130 uM/m2/yr) in the Landsort Deep allows for a more continuous formation of Mn carbonates compared to the other Deeps. However, as noted earlier in the manuscript, pore water geochemical fluxes are quite variable. For instance, Bruegmann et al. (1998, Applied Geochemistry 13, 359-368) observed a diffusive benthic Mn flux of 180 uM/m2/yr in the Gotland Deep in 1994 whereas Heiser et al. (2001) reported a flux of 70 uM/m2/yr for 1997. Lenz et al. seem to assume that the high(er) Mn flux is a permanent feature in the Landsort Deep but do not provide any mechanistic explanation for this assumption. Note also that the Mn profile of the Landsort Deep site does not have a bottom water value, which makes me wonder how the 'very high' Mn flux was calculated.

We modified this section. See point 22 of reviewer #4.

2. Further below, the authors note the presence of MnS in sediments of the Landsort Deep and attribute its occurrence to higher rates of sulfate reduction, possibly enabled by a higher organic carbon flux. The coincidence of organic matter (or Br) and Mo enrichments is a common feature in marine systems (see e.g., Algeo &

Lyons,2006 Paleoceanography 21, PA1016). But is the organic matter flux in the Landsort Deep generally higher compared to the other Deeps? What is the ultimate reason for the higher Mn and organic carbon flux? Is there independent evidence for seasonal variability in the organic matter flux and, if yes, what is the reason for this variability?
Hydrodynamic (frequency or intensity of inflow events), bathymetric (water depth, aerial extent) and other factors should be evaluated here in order to better characterize the environment in which abundant MnS may form.

The Landsort Deep is the deepest basin in the Baltic Sea and its geometry is known to make it an excellent sediment trap (e.g. Expedition 347 Scientists, 2014). As a consequence, sediment deposition rates in this Deep are much higher than elsewhere in the basin. While the Holocene sediments can be obtained using a 4 of 5 m long gravity corer in the other Deeps (e.g. Jilbert and Slomp, 2013), capturing the same Holocene interval in the Landsort Deep required IODP drilling. A detailed discussion of the possible hydrodynamics contributing to this trapping of sediment lies outside the scope of this paper. That the organic matter flux to the sediment in the Landsort Deep is higher is also evident from the pore water data presented here: the ammonium and alkalinity values are significantly higher than in other basins. Seasonal variability in primary productivity in the Baltic Sea is well-described in the literature, e.g. Bianchi et al. 2002.

We have now added more details on the depositional environment in the Landsort Deep and how it differs from the other basins. See response 22 to reviewer #4 above.

We have also added a reference to the seasonality of organic matter inputs:
9903 line 2. "[...] organic matter flux (Fig. 5). Primary productivity in the Baltic Sea is known to vary seasonally (Bianchi et al., 2002; Fennel , 1995)."

3. Page 9904, below Line 3: For mechanistic reasons I feel the change in Mn burial efficiency should be discussed in the context of the decreasing duration and frequency of inflow events rather than the expansion or intensification of anoxia (see Scholz et al., 2013, Chemical Geology). Prior to 1980 the inflow events were typically more extended or took place as groups of events and the corresponding Mn carbonate layers are more pronounced compared to the more recent ones. Partial burial of Mn (oxyhydr)oxides during long-lasting events likely increased the residence time/concentration of Mn in the pore water and thus the extent of reaction with upward diffusing carbonate. By contrast, if anoxia returns rapidly after a single event, most of the Mn oxide still resides at the sediment surface or in the fluffy mud layer, which is why much or most of it may re-dissolve and become recycled into the bottom water through either re-suspension (Heiser et al., 2001, Marine Geology) or diffusion (present study). It is important to note in this context that because of the complex interaction between climate-controlled freshwater runoff and seawater inflow (i.e., haline stratification) as well as nutrient dynamics,

the duration/frequency of inflow events is not the exact reverse of the intensity of anoxia.

We maintain that the degree of anoxia is the factor directly responsible for the extent of Mn burial after inflows, because it is this which determines the exposure of recently precipitated Mn oxides to hydrogen sulfide. However, the frequency of inflows (which has indeed declined since 1980) does play a role in the prevailing degree of anoxia, along with nutrient inputs and climatic factors. The best currently available simulation of the eutrophication and associated oxygen depletion of the Baltic during the 20th century (Gustafsson et al., 2012) shows that the shift to severely anoxic conditions was driven primarily by accumulated nutrient inputs. In their recent study of water column records for the past century, Carstensen et al. (2014) reached the same conclusion. The change in the inflow regime at 1980 appears to have been coincidental to a rapid decline in oxygen conditions in the deep basins, rather than the driver of it.

As demonstrated by the water column records for the deep basins (Fig. 6), bottom waters were hypoxic and anoxic in between inflows prior to 1980, thus allowing for temporary preservation of Mn oxides in the surface sediment. After 1980, bottom waters were nearly continuously anoxic and sulfidic. The presence of high concentrations of sulfide is expected greatly to reduce the residence time of the Mn oxides formed after an inflow event. This is why we conclude that the hypoxia is likely the cause of the reduction in Mn burial. This is supported by data for previous periods of hypoxia (Lenz et al., 2014).

We agree that we should more explicitly discuss the changes in inflow dynamics over the past decades in the text. We have now added text in section 4.3 to make this clearer. Page 9903 line 18.
“Given the suggested link between Mn burial and inflows, it is important to assess their occurrence. During the past two decades, there were two major (1993, 2003) and several minor inflow events (e.g. 1997) into the Baltic Sea. The event in 1993 was one of the strongest in the last 60 years (Matthäus et al., 2008) and the inflow of 2003 (Feistel et al., 2003) was weaker but still significant enough to reoxygenate the bottom water of the deep basins (Figure 6). However, at F80, Mn sequestration in the sediment […].”

4. Page 9904, below Line 20: Strictly speaking this observation only implies that Mn oxides are not the main burial phase for Mo, which is not surprising given that most of the Mn oxides are dissolved and/or converted to (Mo-poor) carbonate prior to burial. Importantly, Scholz et al. (2013, Chemical Geology) did not claim that Mn oxides are the main carrier phase but that they are likely to contribute to Mo transport into the deep water (see Dellwig et al., 2010, GCA) and to the sediment surface. This contribution likely complicates the Mo isotopic mass balance of the sediments to some extent, which has implications for the use of Mo isotopes as a paleo-redox proxy. Other mechanisms supply Mo to the sediment as well (Naegler et al., 2011, Chemical Geology) and may have become more dominant in the recent

past (Scholz et al., 2011, Chemical Geology). Given that Mo and Mn have a differing mobility/diagenetic behavior under anoxic-sulfidic conditions, the lack of correlation between Mn and Mo in the solid phase does not necessarily imply that Mo has not been shuttled by Mn. In fact, repeated Mn dissolution and re-precipitation coupled to negligible Mn accumulation in the sediment (which is what the authors observe) is actually an important characteristic of the Mn shuttle for Mo (Algeo and Tribovillard, 2009, Chemical Geology 268, 211-225). Moreover, Mo fixation (regardless if shuttled by Mn or Fe (oxyhydr)oxides, Fe sulfides, organic matter or other carrier phases) necessarily requires hydrogen sulfide (e.g., Helz et al., 1996, GCA 60, 3631-3642), which is why the shuttle mechanism itself does not negate the use of Mo accumulation rates as a qualitative redox-indicator. If the authors wish to entirely exclude Mo contributions from Mn and Fe (oxyhydr)oxides, I suggest adding a proper discussion of Mo geochemistry of sediments and pore waters. Otherwise, I suggest deleting this misleading statement.

We have deleted this section.

5. Page 9905, below Line 4: I suggest replacing ‘elevated Mo contents’ with ‘Fe-based redox-proxies’ (e.g., Poulton et al., 2004, Nature 431, 173-177). Mo concentrations are a poor indicator of euxinic conditions, as permanent euxinia in restricted systems typically results in a Mo drawdown from the water column and eventually decreasing Mo concentrations in the sediment (Algeo and Lyons, 2006, Paleoceanography 21, PA1016). In fact, the highest Mo concentrations have been recorded in temporarily euxinic systems (such as Baltic Deeps) where regular inflow of oxic (and Mo-replete) water occurs (Algeo and Lyons, 2006, Paleoceanography 21, PA1016). Moreover, open-marine and non-euxinic systems may display very high Mo concentrations as well (e.g., Scholz et al., 2011, GCA 75, 7257-7276).

We refer the reviewer to Figure 4 in the paper by Jilbert and Slomp (2013b). This figure shows that Mo sequestration in the Baltic Sea during hypoxic events is comparable to that in Saanich Inlet on Vancouver Island (British Columbia, Canada), which is considered to undergo negligible basin reservoir effects (Algeo and Lyons, 2006). This demonstrates that Mo is not affected by reservoir effects in the Baltic Sea and can be used as a redox indicator. This is confirmed by the clear relationship between Mo/Al and $C_{org}$/P in these sediments, as presented in the same paper.

6. Page 9905, below Line 11: The deep Mn flux in the Landsort Deep is related to Mn carbonate dissolution and thus a remnant of intermittently oxic/anoxic conditions. Therefore, the presence of Mn enrichments in the sediments does not indicate permanent anoxia but a transitional state, which does not negate the Calvert and Pedersen model. Instead of pointing out the need for multiple proxies (which is kind of common sense anyway), the authors could develop the sedimentary finger print of the Landsort Deep towards an indicator for the transitional state between intermittent and permanent anoxia.

This has been removed from the manuscript. See reply 22 to reviewer #4.

We have kept the statement about multiple redox proxies, because we consider it to be important.

7. Page 9905, line 26: I would argue that the decreased abundance/intensity of Mn enrichments in most of the Deeps is a pretty accurate reflection of the reduced frequency and duration of inflow events since the late 1970s.

See our reply to comment 3 above.

Minor comments:

8. I think it would be generally more useful to use the full names of the basins instead of acronyms for the sampling stations in the discussion.

Where possible, we have added the full names of the basins as suggested.

9. Page 9894, Line 25: I doubt that pH measurements after 30 minutes of centrifuging yield meaningful results.

We refer to our reply to comment #16 of reviewer #4.

10. Page 9900, Line 11: Could add 'Scholz et al., 2013, Chemical Geology'.

We have added a reference to the work of Scholz et al. 2013 and Scholz et al. 2014.

11. Page 9901, Line 8: Replace 'conclude' with 'suggest'.

We now write "*It is likely that*"

12. Page 9905, Line 5: Delete 'sediment' before 'euxinia'. By definition, euxinia refers to the water column.

We have replaced "*sediment*" by "*water column*"

13. Table 1 and 2: Add the names of basins to the stations.

We have made the suggested change.

14. Fig. 1: Add the names of all basins to the cross section.

We have added the names of the Fårö Deep and northern Gotland Deep to the cross section.

**Additional remarks by the authors:**

Besides the changes in relation to the reviews we also apply minor changes to improve the readability of the manuscript. All changes are visible in the submitted version with track changes.

## References

Adelson, J. M., Helz, G. R., and Miller, C. V.: Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake Bay sediments, Geochim Cosmochim Acta, 65, 237-252, 2001.
Algeo, T. J. and Lyons, T. W.: Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions, Paleoceanography, 21, 2006.
Anschutz, P., Blanc, G., and Stille, P.: Origin of fluids and the evolution of the Atlantis II deep hydrothermal system, Red Sea: Strontium isotope study, Geochim Cosmochim Acta, 59, 4799-4808, 1995.
Beal, E. J., House, C. H., and Orphan, V. J.: Manganese- and Iron-Dependent Marine Methane Oxidation, Science, 325, 184-187, 2009.
Berner, R. A., Scott, M. R., and Thomlinson, C.: Carbonate alkalinity in the pore waters of anoxic marine sediments, Limnol Oceanogr, 15, 544-549, 1970.
Bianchi, T. S., Rolff, C., Widbom, B., and Elmgren, R.: Phytoplankton Pigments in Baltic Sea Seston and Sediments: Seasonal Variability, Fluxes, and Transformations, Estuar Coast Shelf Sci, 55, 369-383, 2002.
Boesen, C. and Postma, D.: Pyrite formation in anoxic environments of the Baltic, Am J Sci, 288, 575-603, 1988.
Böttcher, M. E.: Manganese (II) partitioning during experimental precipitation of rhodochrosite–calcite solid solutions from aqueous solutions, Mar Chem, 62, 287-297, 1998.
Cai, W.-J. and Reimers, C. E.: The development of pH and pCO2 microelectrodes for studying the carbonate chemistry of pore waters near the sediment-water interface, Limnol Oceanogr, 38, 1762-1773, 1993.
Calvert, S. and Pedersen, T.: Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological record, Mar Geol, 113, 67-88, 1993.
Calvert, S. and Pedersen, T.: Sedimentary geochemistry of manganese; implications for the environment of formation of manganiferous black shales, Econ Geol, 91, 36-47, 1996.
Canfield, D. E. and Thamdrup, B.: Towards a consistent classification scheme for geochemical environments, or, why we wish the term 'suboxic' would go away, Geobiology, 7, 385-392, 2009.
Carman, R. and Rahm, L.: Early diagenesis and chemical characteristics of interstitial water and sediments in the deep deposition bottoms of the Baltic proper, J Sea Res, 37, 25-47, 1997.

Carstensen, J., Andersen, J. H., Gustafsson, B. G., and Conley, D. J.: Deoxygenation of the Baltic Sea during the last century, PNAS, 111, 5628-5633, 2014.
Dellwig, O., Leipe, T., März, C., Glockzin, M., Pollehne, F., Schnetger, B., Yakushev, E. V., Böttcher, M. E., and Brumsack, H.-J.: A new particulate Mn–Fe–P-shuttle at the redoxcline of anoxic basins, Geochim Cosmochim Acta, 74, 7100-7115, 2010.
Dellwig, O., Schnetger, B., Brumsack, H.-J., Grossart, H.-P., and Umlauf, L.: Dissolved reactive manganese at pelagic redoxclines (part II): Hydrodynamic conditions for accumulation, J Mar Syst, 90, 31-41, 2012.
Deng, S., Dong, H., Lv, G., Jiang, H., Yu, B., and Bishop, M. E.: Microbial dolomite precipitation using sulfate reducing and halophilic bacteria: Results from Qinghai Lake, Tibetan Plateau, NW China, Chem Geol, 278, 151-159, 2010.
Diaz, R. J. and Rosenberg, R.: Spreading dead zones and consequences for marine ecosystems, Science, 321, 926-929, 2008.
Egger, M., Rasigraf, O., Sapart, C. J., Jilbert, T., Jetten, M. S. M., Röckmann, T., van der Veen, C., Bândă, N., Kartal, B., Ettwig, K. F., and Slomp, C. P.: Iron-Mediated Anaerobic Oxidation of Methane in Brackish Coastal Sediments, Environ Sci Technol, 49, 277-283, 2015.
Emerson, S., Jacobs, L., and Tebo, B.: The Behavior of Trace Metals in Marine Anoxic Waters: Solubilities at the Oxygen-Hydrogen Sulfide Interface. In: Trace Metals in Sea Water, Wong, C. S., Boyle, E., Bruland, K., Burton, J. D., and Goldberg, E. (Eds.), NATO Conference Series, Springer US, 1983.
Erickson, B. E. and Helz, G. R.: Molybdenum(VI) speciation in sulfidic waters:: Stability and lability of thiomolybdates, Geochim Cosmochim Acta, 64, 1149-1158, 2000.
Expedition 347 Scientists: Baltic Sea Basin Paleoenvironment: paleoenvironmental evolution of the Baltic Sea Basin through the last glacial cycle. , IODP Prel. Rept., 347, 2014.
Feistel, R., Nausch, G., Mohrholz, V., Lysiak-Pastuszak, E., Seifert, T., Matthaus, W., Kruger, S., and Hansen, I. S.: Warm waters of summer 2002 in the deep Baltic Proper, Oceanologia, 45, 571-592, 2003.
Fennel, W.: A model of the yearly cycle of nutrients and plankton in the Baltic Sea, J Mar Syst, 6, 313-329, 1995.
Fonselius, S. and Valderrama, J.: One hundred years of hydrographic measurements in the Baltic Sea, J Sea Res, 49, 229-241, 2003.
Gustafsson, B. G., Schenk, F., Blenckner, T., Eilola, K., Meier, H. M., Müller-Karulis, B., Neumann, T., Ruoho-Airola, T., Savchuk, O. P., and Zorita, E.: Reconstructing the development of Baltic Sea eutrophication 1850–2006, Ambio, 41, 534-548, 2012.
Heiser, U., Neumann, T., Scholten, J., and Stüben, D.: Recycling of manganese from anoxic sediments in stagnant basins by seawater inflow: A study of surface sediments from the Gotland Basin, Baltic Sea, Mar Geol, 177, 151-166, 2001.
Helz, G. R., Bura-Nakić, E., Mikac, N., and Ciglenečki, I.: New model for molybdenum behavior in euxinic waters, Chem Geol, 284, 323-332, 2011.
Holtermann, P. L. and Umlauf, L.: The Baltic Sea Tracer Release Experiment: 2. Mixing processes, Journal of Geophysical Research: Oceans, 117, C01022, 2012.

Huckriede, H. and Meischner, D.: Origin and environment of manganese-rich sediments within black-shale basins, Geochim Cosmochim Acta, 60, 1399-1413, 1996.

Jakobsen, R. and Postma, D.: Formation and solid solution behavior of Ca-rhodochrosites in marine muds of the Baltic deeps, Geochim Cosmochim Acta, 53, 2639-2648, 1989.

Jilbert, T., Conley, D. J., Gustafsson, B. G., Funkey, C. P., and Slomp, C. P.: Glacio-isostatic control on hypoxia in a high-latitude shelf basin, Geology, 43, 427-430, 2015.

Jilbert, T. and Slomp, C. P.: Iron and manganese shuttles control the formation of authigenic phosphorus minerals in the euxinic basins of the Baltic Sea, Geochim Cosmochim Acta, 107, 155-169, 2013a.

Jilbert, T. and Slomp, C. P.: Rapid high-amplitude variability in Baltic Sea hypoxia during the Holocene, Geology, 41, 1183-1186, 2013b.

Jilbert, T., Slomp, C. P., Gustafsson, B. G., and Boer, W.: Beyond the Fe-P-redox connection: preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles, Biogeosciences, 8, 1699-1720, 2011.

Katsikopoulos, D., Fernández-González, Á., and Prieto, M.: Precipitation and mixing properties of the “disordered” (Mn,Ca)CO3 solid solution, Geochim Cosmochim Acta, 73, 6147-6161, 2009.

Kulik, D. A., Kersten, M., Heiser, U., and Neumann, T.: Application of Gibbs energy minimization to model early-diagenetic solid-solution aqueous-solution equilibria involving authigenic rhodochrosites in anoxic Baltic Sea sediments, Aquat Geochem, 6, 147-199, 2000.

Lenz, C., Behrends, T., Jilbert, T., Silveira, M., and Slomp, C. P.: Redox-dependent changes in manganese speciation in Baltic Sea sediments from the Holocene Thermal Maximum: An EXAFS, XANES and LA-ICP-MS study, Chem Geol, 370, 49-57, 2014.

Lepland, A. and Stevens, R. L.: Manganese authigenesis in the Landsort Deep, Baltic Sea, Mar Geol, 151, 1-25, 1998.

Löffler, A.: The importance of particles for the distribution of trace metals in the Baltic Sea, especially under changing redox conditions in the central Baltic deep basins., Meereswissenschaftliche Berichte Warnemünde, 27, 153, 1997.

Luther III, G. W., Sundby, B., Lewis, B. L., Brendel, P. J., and Silverberg, N.: Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen, Geochim Cosmochim Acta, 61, 4043-4052, 1997.

Madison, A. S., Tebo, B. M., and Luther, G. W.: Simultaneous determination of soluble manganese (III), manganese (II) and total manganese in natural (pore) waters, Talanta, 84, 374-381, 2011.

Manheim, F. T.: A geochemical profile in the Baltic Sea, Geochim Cosmochim Acta, 25, 52-70, 1961.

Matthäus, W., Nehring, D., Feistel, R., Nausch, G., Mohrholz, V., and Lass, H.-U.: The Inflow of Highly Saline Water into the Baltic Sea. In: State and Evolution of the Baltic Sea, 1952–2005, John Wiley & Sons, Inc., 2008.

Mercone, D., Thomson, J., Abu-Zied, R., Croudace, I., and Rohling, E.: High-resolution geochemical and micropalaeontological profiling of the most recent eastern Mediterranean sapropel, Mar Geol, 177, 25-44, 2001.

Mort, H. P., Slomp, C. P., Gustafsson, B. G., and Andersen, T. J.: Phosphorus recycling and burial in Baltic Sea sediments with contrasting redox conditions, Geochim Cosmochim Acta, 74, 1350-1362, 2010.

Mouret, A., Anschutz, P., Lecroart, P., Chaillou, G., Hyacinthe, C., Deborde, J., Jorissen, F., Deflandre, B., Schmidt, S., and Jouanneau, J.-M.: Benthic geochemistry of manganese in the Bay of Biscay, and sediment mass accumulation rate, Geo-Mar Lett, 29, 133-149, 2009.

Neretin, L. N., Pohl, C., Jost, G., Leipe, T., and Pollehne, F.: Manganese cycling in the Gotland Deep, Baltic Sea, Mar Chem, 82, 125-143, 2003.

Neumann, T., Heiser, U., Leosson, M. A., and Kersten, M.: Early diagenetic processes during Mn-carbonate formation: Evidence from the isotopic composition of authigenic Ca-rhodochrosites of the Baltic Sea, Geochim Cosmochim Acta, 66, 867-879, 2002.

Pakhomova, S. and Yakushev, E. V.: Manganese and Iron at the Redox Interfaces in the Black Sea, the Baltic Sea, and the Oslo Fjord. In: Chemical Structure of Pelagic Redox Interfaces, Yakushev, E. V. (Ed.), The Handbook of Environmental Chemistry, Springer Berlin Heidelberg, 2013.

Pakhomova, S. V., Hall, P. O., Kononets, M. Y., Rozanov, A. G., Tengberg, A., and Vershinin, A. V.: Fluxes of iron and manganese across the sediment–water interface under various redox conditions, Mar Chem, 107, 319-331, 2007.

Parkhurst, D. L. and Appelo, C.: User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, 1999. 1999.

Passier, H. F., Böttcher, M. E., and de Lange, G. J.: Sulphur Enrichment in Organic Matter of Eastern Mediterranean Sapropels: A Study of Sulphur Isotope Partitioning, Aquat Geochem, 5, 99-118, 1999.

Pohl, C. and Hennings, U.: The coupling of long-term trace metal trends to internal trace metal fluxes at the oxic‐anoxic interface in the Gotland Basin (57° 19, 20′ N; 20° 03, 00′ E) Baltic Sea, J Mar Syst, 56, 207-225, 2005.

Scholz, F., McManus, J., Mix, A. C., Hensen, C., and Schneider, R. R.: The impact of ocean deoxygenation on iron release from continental margin sediments, Nat. Geosci., 7, 433-437, 2014.

Scholz, F., McManus, J., and Sommer, S.: The manganese and iron shuttle in a modern euxinic basin and implications for molybdenum cycling at euxinic ocean margins, Chem Geol, 355, 56-68, 2013.

Slomp, C. P., Malschaert, J. F. P., Lohse, L., and VanRaaphorst, W.: Iron and manganese cycling in different sedimentary environments on the North Sea continental margin, Cont Shelf Res, 17, 1083-1117, 1997.

Sternbeck, J. and Sohlenius, G.: Authigenic sulfide and carbonate mineral formation in Holocene sediments of the Baltic Sea, Chem Geol, 135, 55-73, 1997.

Suess, E.: Mineral phases formed in anoxic sediments by microbial decomposition of organic matter, Geochim Cosmochim Acta, 43, 339-352, 1979.

Turnewitsch, R. and Pohl, C.: An estimate of the efficiency of the iron-and manganese-driven dissolved inorganic phosphorus trap at an oxic/euxinic water column redoxcline, Global Biogeochem Cycles, 24, GB4025, 2010.

Ulfsbo, A., Hulth, S., and Anderson, L. G.: pH and biogeochemical processes in the Gotland Basin of the Baltic Sea, Mar Chem, 127, 20-30, 2011.

Wang, Y. and Van Cappellen, P.: A multicomponent reactive transport model of early diagenesis: Application to redox cycling in coastal marine sediments, Geochim Cosmochim Acta, 60, 2993-3014, 1996.

Yakushev, E. V., Kuznetsov, I. S., Podymov, O. I., Burchard, H., Neumann, T., and Pollehne, F.: Modeling the influence of oxygenated inflows on the biogeochemical structure of the Gotland Sea, central Baltic Sea: Changes in the distribution of manganese, Comput Geosci, 37, 398-409, 2011.

# Are recent changes in sediment manganese sequestration in the euxinic basins of the Baltic Sea linked to the expansion of hypoxia?

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## Abstract

Expanding hypoxia in the Baltic Sea over the past century has led to anoxic and sulfidic (euxinic) deep basins that are only periodically ventilated by inflows of oxygenated waters from the North Sea. In this study, we investigate the potential consequences of the expanding hypoxia for manganese (Mn) burial in the Baltic Sea using a combination of pore water and sediment analyses of dated sediment cores from 8 locations. Diffusive fluxes of dissolved Mn from sediments to overlying waters at oxic, hypoxic and euxinic sites are in line with an active release of Mn from these areas. Although the fluxes are significant (ranging up to ca. 240 µmol m$^{-2}$ d$^{-1}$), published water column data suggest that the benthic release of Mn is small when compared to the large pool of Mn already present in the hypoxic and anoxic water column. Our results highlight two modes of Mn carbonate formation in sediments of the deep basins. In the Gotland Deep area, Mn carbonates likely form from Mn oxides that are precipitated from the water column directly following North Sea inflows. In the Landsort Deep, in contrast, Mn carbonate and Mn sulfide layers appear to form independent of inflow events, and are possibly related to the much larger and continuous input of Mn oxides linked to sediment focusing. While formation of Mn enrichments in the Landsort Deep continues to the present, this does not hold for the Gotland Deep area. Here, a recent increase in euxinia, as

**Gelöscht:** well-

**Gelöscht:** and

**Gelöscht:** However,

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**Gelöscht:** with pore water Mn produced in deeper layers of the sediment acting as a key Mn source.

**Gelöscht:** d

evident from measured bottom water sulfide concentrations and elevated sediment molybdenum (Mo), coincides with a decline in sediment Mn. Sediment analyses also reveal that recent inflows of oxygenated water (since ca. 1995) are no longer consistently recorded as Mn carbonate layers. We hypothesize that the recent rise in sulfate reduction rates linked to eutrophication and decline in reactive Fe input to these basins, as recorded by sediment Fe/Al ratios, has led to higher sulfide availability near the sediment-water interface after inflow events. As a consequence, the Mn oxides may be reductively dissolved more rapidly than in the past and Mn carbonates may no longer form. Using a simple diagenetic model for Mn dynamics in the surface sediment, we demonstrate that an enhancement of the rate of reduction of Mn oxides is in line with such a scenario. Our results have important implications for the use of Mn carbonate enrichments as a redox proxy in marine systems.

**Gelöscht:** goes hand in hand

**Gelöscht:** and

**Gelöscht:** We postulate that, because of the quicker return of high sulfide concentrations in the water column, the reduction of Mn oxides following an inflow has become so rapid that the $Mn^{2+}$ is released to the water column before Mn carbonates can form.

## 1 Introduction

Manganese (Mn) enrichments in brackish and marine sedimentary deposits can be used as an indicator of redox changes in the overlying waters (e.g. Calvert and Pedersen, 1993). In anoxic settings, Mn-enrichments are typically assumed to consist of Mn carbonates, which are associated with calcium and can contain other impurities (e.g. Jakobsen and Postma, 1989; Manheim, 1961; Sternbeck and Sohlenius, 1997; Suess, 1979). For simplicity, in this study these phases are collectively referred to as Mn carbonates, despite their obvious greater complexity and heterogeneity. Mn carbonate minerals are suggested to form from Mn oxides deposited during periods of bottom water oxygenation (Calvert and Pedersen, 1996; Huckriede and Meischner, 1996), with $Mn^{2+}$ availability thought to be the key control (Neumann et al., 2002). However, sediment Mn data for both the Landsort Deep in the Baltic Sea (Lepland and Stevens, 1998) and the Black Sea (Lyons and Severmann, 2006) indicate that Mn enrichments may also form in sediments overlain by continuously anoxic bottom waters. In the Landsort Deep, these enrichments consist of both Mn carbonates and Mn sulfides (Lepland and Stevens, 1998; Suess, 1979). The formation of Mn carbonate is assumed to be driven by an exceptionally high alkalinity. Mn sulfides form when $H_2S$ exceeds Fe availability (Böttcher and Huckriede, 1997; Lepland and Stevens, 1998). 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). Finally, Mn enrichments may also

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form in sediments overlain by oxic bottom waters upon increased input and precipitation of Mn oxides and transformation to Mn carbonate during burial (e.g. MacDonald and Gobeil, 2012). A better understanding of the various modes of formation of sedimentary Mn and the link with variations in bottom water redox conditions is essential when interpreting Mn enrichments in geological deposits (e.g. Calvert and Pedersen, 1996; Huckriede and Meischner, 1996; Jones et al., 2011; Meister et al., 2009).

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Redox-dependent dynamics of Mn have been studied extensively in the Baltic Sea (e.g. Huckriede and Meischner, 1996; Lepland and Stevens, 1998; Neumann et al., 2002) and are of interest because of the large spatial and temporal variations in bottom water oxygen conditions over the past century that are particularly well documented since the 1970's (Fonselius and Valderrama, 2003). Besides providing evidence for sporadic inflows of oxygenated saline water from the North Sea that affect brackish bottom waters in all deep basins (Matthäus and Franck, 1992; Matthäus et al. 2008), the available hydrographic data indicate a major expansion of the hypoxic area in the Baltic Sea linked to increased eutrophication (Carstensen et al., 2014; Conley et al., 2009; Gustafsson et al., 2012; Savchuk et al., 2008). While the shallower areas in the Baltic Sea are now seasonally hypoxic, the deep basins all show a major shift towards anoxic and sulfidic (euxinic) conditions around 1980 (Fonselius and Valderrama, 2003; Mort et al., 2010). These basin-wide changes in redox conditions likely had a major impact on both the sources and sinks of sediment Mn in the Baltic Sea.

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

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During the expansion of hypoxia and anoxia, as observed in the Baltic Sea over the past century (Conley et al., 2009), the Mn shuttle likely became more efficient in transporting Mn to deeper, euxinic basins because of decreased trapping of Mn in oxygenated surface sediments (Lyons and Severmann, 2006). However, during an extended period of hypoxia and anoxia, sediments in hypoxic areas may become depleted of Mn oxides, thus reducing the strength of the Mn shuttle from oxic and hypoxic shelves to the deep basins. In addition, the formation rate of authigenic Mn minerals in the sediment at deep basin sites may change in response to bottom water hypoxia and anoxia. If release of dissolved Mn$^{2+}$ from Mn oxides – formed at the sediment surface following inflows of oxygenated North Sea water – is the dominant control for Mn carbonate formation in the sediment as suggested for the Gotland Deep (Neumann et al., 2002), expanding bottom water anoxia might allow Mn oxides to be reduced in the water column and at the sediment-water interface, precluding conversion to Mn carbonates. This mechanism was recently invoked to explain the lack of Mn carbonates in the sediment during periods of bottom water euxinia in the Gotland Deep during the Holocene Thermal Maximum (Lenz et al., 2014). If alkalinity is the key control, however, as suggested for the Landsort Deep (Lepland and Stevens, 1998), Mn sequestration would be expected to be similar or increase due to higher rates of sulfate reduction.

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

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# 2 Materials and Methods

## 2.1 Study area

Fine-grained sediments from 8 locations in the southern and central Baltic Sea were collected during 4 cruises between 2007 and 2011 (Figure 1, Table 1) using a multi-corer. The sites differ with respect to their water depths and their present-day bottom water redox conditions. The Fladen and LF1 sites are located in the Kattegat and along the eastern side of the Gotland Deep, respectively, and are fully oxic, whereas site BY5 in the Bornholm Basin is seasonally hypoxic (Jilbert et al., 2011; Mort et al., 2010). The remaining stations, LF3, LL19, BY15 (Gotland Basin), F80 (Fårö Deep) and LD1 (Landsort Deep), are situated below the redoxcline, which was located between 80 and 120 m water depth at the time of sampling. Therefore, bottom waters at these sites were all anoxic and sulfidic (euxinic). The latter 4 sites are located in the deep central basins of the Baltic Sea, at water depths ranging from 169 m at LL19 to 416 m at LD1. Water column data for oxygen and hydrogen sulfide for LL19 and LD1 (as recorded at LL23 as a nearby station) are available from the ICES Dataset on Ocean Hydrology (2014). The sampling, and selected pore water and sediment analyses for many of our sites have been described previously (Mort et al., 2010, Jilbert et al., 2011; Jilbert and Slomp, 2013a). For completeness, all procedures are described again below.

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## 2.2 Bottom water and pore water analyses

A bottom water sample was taken from the water overlying the sediment in each multicore as soon as possible after core collection. At each site, sediment multi-cores (<50 cm, 10 cm i.d.) were either immediately sectioned in a $N_2$-filled glovebox at in-situ temperature or sampled with syringes through pre-drilled holes in the core liner. A small portion of each sample was stored at 5°C or -20°C in gas-tight jars for sediment analyses. The remaining sediment was centrifuged (10-30 min.; 2500 g) in 50 ml greiner tubes to collect pore water. Both the pore water and a bottom water sample were filtered (0.45 µm pore size) and subdivided for later laboratory analyses. All pore water handling prior to storage was performed in a $N_2$ atmosphere. A subsample of 0.5 ml was directly transferred to a vial with 2 ml of a 2% Zn-acetate solution for analysis of hydrogen sulfide. Sulfide concentrations were determined by complexation of the ZnS precipitate using phenylenediamine and ferric chloride (Strickland and Parsons, 1972). Subsamples for total Mn, Fe, Ca and S were acidified with either $HNO_3$ (Fladen, BY5) or HCl (all other stations) and stored at 5°C until further analysis with

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Optima 3000; relative precision and accuracy as established by standards (ISE-921) and duplicates were always <5%). Hydrogen sulfide was assumed to be released during the initial acidification, thus S is assumed to represent $SO_4^{2-}$ only. Total Mn and Fe are assumed to represent $Mn^{2+}$ and $Fe^{2+}$ although in the former case some $Mn^{3+}$ may also be included (Madison et al., 2011). Subsamples for $NH_4$ were frozen at -20°C until spectrophotometric analysis using the phenol hypochlorite method (Riley, 1953). A final subsample was used to determine the pH with a pH electrode and meter (Sentron). Note that degassing of $CO_2$ may impact ex-situ pH measurements and may lead to a rise in pH (Cai and Reimers, 1993). As a consequence, our pH values should be seen as an approximation only. The total alkalinity was then determined by titration with 0.01 M HCl. All colorimetric analyses were performed with a Shimadzu spectrophotometer. Replicate analyses indicated that the relative error for the pore water analyses was generally <10 %.

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At four deep basin sites (LL19, BY15, F80, LD1), a second multicore was sampled and analysed for methane as described by Jilbert and Slomp (2013a). Briefly, a cutoff syringe was inserted into a pre-drilled, taped hole at 1.5 cm intervals directly after core collection. Precisely 10 ml wet sediment was extracted from each hole and transferred immediately to a 65 ml glass bottle filled with saturated sodium chloride (NaCl) solution. This bottle was then closed with a rubber stopper and screwcap, and a headspace of 10 ml $N_2$ gas was inserted. Methane concentrations in the headspace of the glass bottles were determined by injection of a subsample into a Thermo Finnigan Trace GC gas chromatograph (flame ionization detector, Restek Q-PLOT column of 30 m length, 0.32 mm internal diameter, oven temperature 25°C). Data were then back-calculated to the original pore water concentrations using the measured porosities (see Section 2.3). Because of degassing, which is unavoidable at sites with very high $CH_4$ concentrations, the $CH_4$ profile at LD1 is considered to be less reliable

## 2.3 Sediment analyses

Sediment samples were freeze-dried and water contents and porosities were calculated from the weight loss, assuming a sediment density of 2.65 g cm$^{-3}$. Sediments were then ground in an agate mortar in a $N_2$ or argon-filled glovebox. From each sediment sample, aliquots for several different analyses were taken. For total organic carbon (TOC) analyses, 0.3 g of sediment was decalcified with 1M HCl and the C content was determined with a Fisons NA 1500 CNS analyser (van Santvoort et al., 2002). Based on the analyses of laboratory reference

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materials and replicates, the relative error of the TOC measurements was generally less than 5%. Total sediment contents of S, Mn, Ca, Fe, Al and Mo were determined by ICP-OES, after dissolution of 0.125 g of sample with an $HF/HClO_4/HNO_3$ mixture in closed Teflon bombs at 90°C, followed by evaporation of the solution and redissolution of the remaining gel in 1M $HNO_3$ (Passier et al., 1999). The accuracy and precision of the measurements were established by measuring laboratory reference materials (ISE-921 and in-house standards) and sample replicates; relative errors were <5% for all reported elements. The detection limits of ICP-OES for Mn, Mo, Ca, Fe, Al and S in the $HNO_3$ solution are 0.6, 14, 5, 6 and 24 µg kg$^{-1}$ and 0.28 mg kg$^{-1}$ respectively. All elemental concentrations in the sediment were corrected for the weight of the salt in the pore water using the ambient salinity and porosity.

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Age models based on $^{210}$Pb analyses for 6 multi-cores used in this study have been previously published. For details, we refer the reader to the relevant studies: Fladen and BY5 (Mort et al., 2010), LF1 and LF3 (Jilbert et al., 2011), LL19 (Zillén et al., 2012) and BY15 (Jilbert and Slomp, 2013b). A new $^{210}$Pb age model was constructed for LD1. Samples from the Landsort Deep (LD1) were analyzed with a Canberra BeGe gamma ray spectrometer at Utrecht University. The samples were freeze-dried, homogenized, and transferred into vent-free petri dishes, which were sealed in polyethylene bags and stored for 2 weeks before measuring. Each sample was measured until 200-250 $^{210}$Pb gamma-ray counts were reached. For the age determination a constant rate of supply model (Appleby and Oldfield, 1983) was implemented using a background estimated from the mean counts of $^{214}$Pb and $^{214}$Bi. For further details on the age models and the $^{210}$Pb data for LD1, we refer to the supplementary information Appendix A. The age model for the site in the Fårö Deep (F80) was constructed using high resolution Mo and Mn data. In 2013, an extra sediment core from this station was taken. Mini sub-cores as described in section 2.4 were embedded in Spurr´s epoxy resin and measured by Laser Ablation - Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) line scanning. The fluctuations in Mo/Al and Mn/Al ratios were coupled to the instrumental records of bottom water oxygen conditions. The 2009 multicore profiles were subsequently tuned to the dated profiles from 2013 (see Appendix A for more details).

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## 2.4 Microanalysis

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

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

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

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).

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## 2.5 Flux calculations

The diffusive flux of manganese across the sediment-water interface ($J_{sed}$) was calculated from the concentration gradient in the pore water over the upper 0.25 to 2.5 cm of the sediment with Fick's first law for 6 sites:

$$J_{sed} = -\phi D_{sed} \frac{dC_{Mn2+}}{dx} \qquad (1)$$

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

$$D_{sed} = \frac{D_{SW}}{(1-\ln\phi^2)} \qquad (2)$$

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

## 2.6 Saturation state

Thermodynamic equilibrium calculations were performed for the pore water of LF3, LL19, BY15, F80 and LD1 using version 3.1.1 of the computer program PHREEQC (Parkhurst and Appelo, 1999) with the LLNL database. Our calculations should be seen as approximations with the main purpose of providing a comparison to previous calculations by Carman and Rahm (1997) and Heiser et al. (2001) to assess whether there are any indications for a change in saturation state of the pore water between inflows. The LLNL database does not contain the authigenic carbonate phases present in the Baltic Sea. However, data from the literature (Jakobsen and Postma, 1989; Sternbeck and Sohlenius, 1997; Lepland and Stevens, 1998; Huckriede and Meischner 1996; Kulik et al., 2000) suggest that Baltic carbonates are predominantly Mn carbonates with a substantial contribution of Ca. Therefore, an approximation of the solubility product of (Mn, Ca) $CO_3$ solid solutions was generated using the equations given in Katsikopoulos et al. (2009). The stoichiometric solubility product ($K_{st}$) was calculated using $Mn_{0.74}Ca_{0.26}CO_3$ (Kulik et al 2000) as a common ratio measured for (Mn, Ca) $CO_3$ solid solutions in Baltic Sea sediments.

An equilibrium constant pK of 0.377 (Emerson et al. 1983) was used for Mn sulfide. The solubility of iron sulfide from Rickard (2006) was added to the calculations as well as $MnHS^+$ as a solute (Luther et al., 1996) because it is likely abundant in pore water in sulfidic sediments (Heiser et al., 2001). At sites LF3 and LD1, $Fe^{2+}$ was below the detection limit and the calculation of the saturation state with respect to FeS could not be performed. Carbonate alkalinity was calculated from titration alkalinity as described by Carman and Rahm (1997).

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$J_{sed} = -\varphi * D_{sed} * (\delta C/\delta x)$ ¶
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$D_{sed} = D^{SW} / 1 – \ln(\varphi^2)$¶
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## 2.7 Diagenetic model for Mn

A simple diagenetic model for Mn was developed to assess the potential effect of changes in the kinetics of reductive dissolution of Mn oxides to dissolved $Mn^{2+}$ and subsequent Mn carbonate formation in Baltic Sea surface sediments following an inflow event. Our modeling is generic and addresses this research question only. Therefore, we do not attempt to describe all the relevant processes potentially controlling Mn carbonate formation in the sediment nor do we focus on a specific location. The model accounts for two biogeochemical processes: reductive dissolution of Mn oxides to $Mn^{2+}$ and precipitation of $Mn^{2+}$ in the form of Mn carbonates. Empirical rate laws for Mn oxide reduction and Mn carbonate formation are assumed, with rates depending on first order rate constants for both processes ($k_{red}$ and $k_{prec}$) and the sediment concentration of Mn oxide and dissolved $Mn^{2+}$, respectively (Berner, 1980; Slomp et al., 1997). Transport is assumed to occur through diffusion ($Mn^{2+}$) and sediment burial ($Mn^{2+}$ and both solids). Porosity ($\phi$), temperature, sediment density ($\rho_S$) and rates of sedimentation ($\omega$) are assumed constant with depth and time. The following differential equations were used:

$$\frac{\partial C_{Mn2+}}{\partial t} = D_{Mn2+}\frac{\partial^2 C_{Mn2+}}{\partial x^2} - \omega\frac{\partial C_{Mn2+}}{\partial x} - k_{prec}C_{Mn2+} + \frac{\rho_s(1-\phi)}{\phi}k_{red}C_{Mnoxide} \quad (3)$$

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

$$\frac{\partial C_{MnCO3}}{\partial t} = -\omega\frac{\partial C_{MnCO3}}{\partial x} + \frac{\phi}{\rho_s(1-\phi)}k_{prec}C_{Mn2+} \quad (5)$$

where $C_{Mn2+}$, $C_{Mnoxide}$ and $C_{MnCO3}$ are the concentrations of dissolved $Mn^{2+}$, Mn oxides and $MnCO_3$, respectively and $D_{Mn2+}$ is the diffusion coefficient of dissolved $Mn^{2+}$ as defined in equation (2). The model code was written in R using the marelac (Soetaert et al., 2010) and ReacTran (Soetaert and Meysman, 2012) packages. The model domain is represented by a one-dimensional grid of 1000 cells that captures the interval from the sediment-water interface to a depth of 1 cm. Environmental parameters typical for surface sediments in the deep basins of the Baltic Sea and boundary conditions were assumed as defined in Table 3.

Here, we assess a scenario for Baltic Sea sediments where Mn oxides are deposited during a period of oxic bottom water conditions for 4 months directly after a North Sea inflow followed by a period of two months in which no Mn oxides are deposited because of the return of bottom water anoxia (Table 3; Section 4.1). We set $k_{prec}$ to 5,000 $yr^{-1}$, placing the maximum rate of Mn carbonate formation in the model calculations in the upper range given by Wang and Van Cappellen (1996). We then assess the response of benthic fluxes of $Mn^{2+}$, rates of formation of Mn carbonate in the sediment and profiles of the various Mn forms to variations in $k_{red}$ when assuming values of either 0.1, 1, 10, 100 or 1000 $yr^{-1}$ during 4 months of the simulation followed by a period of two months with a $k_{red}$ of 1000 $yr^{-1}$ (i.e. representing rapid Mn oxide reduction after the return of anoxic conditions). By varying $k_{red}$, we wish to capture a wide range in the availability of reductants for Mn oxides in the surface sediment. Values of $k_{red}$ estimated for different sedimentary environments overlain by oxic bottom waters in the North Sea range from 0.04 -150 $yr^{-1}$ (Slomp et al., 1997). The slightly wider range assumed here is reasonable because of the more important role of anaerobic pathways of organic matter degradation in deep basin sediments of the Baltic Sea sediments compared to those in the North Sea (e.g. Mort et al., 2010 versus Slomp et al., 1997). To assess the robustness of our results, we also perform the same simulations with even higher $k_{prec}$ values (up to 30,000 $yr^{-1}$).

# 3 Results

At the time of sampling, bottom waters were oxic at the Fladen and LF1 sites in the eastern Gotland Basin, hypoxic at the Bornholm Basin site BY5, and anoxic and sulfidic at all other locations (Table 1). Pore water $Mn^{2+}$ concentrations increase with depth in the sediment at most sites (Figure 2; Appendix B). At the Fladen site, however, $Mn^{2+}$ concentrations decrease again below ca. 5 cm and at the eastern Gotland Basin sites LF1 and LF3, $Mn^{2+}$ concentrations are lower than at other sites. Pore water $Fe^{2+}$ shows a subsurface maximum at the Fladen and LF1 sites, but is low or absent in the pore water at all other sites. Pore water $Ca^{2+}$ concentrations show little change with depth and are in line with the salinity gradient in the Baltic Sea. Alkalinity and ammonium concentrations increase with sediment depth simultaneously with a decline in sulfate. $CH_4$ is present at depth where sulfate is depleted at the sites in the Fårö Deep (F80) and Landsort Deep (LD1) (Appendix B). Similar to $Ca^{2+}$, sulfate concentrations in the bottom water at the different stations are in line with the salinity gradient in the Baltic Sea (Table 1). Concentrations of hydrogen sulfide in the pore water > 2 mM are found at the Fårö Deep and Landsort Deep sites F80 and LD1. The pore waters are supersaturated with respect to Mn carbonate below the surface sediment at the Landsort Deep. The other hypoxic and anoxic sites except LF3 reach saturation only at greater depth. For Mn

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**Gelöscht:** , indicating supersaturation of the pore water with respect to this mineral sulfide, in contrast, supersaturation is only observed at the Landsort Deep site, LD1 (Figure 3) and below 35 cm at site F80. Pore waters were supersaturated with respect to FeS at the sites in the Northern Gotland Basin (LL19), in the Gotland Deep (BY15) and Fårö Deep (F80) (Appendix B). Note that degassing of CO$_2$ during centrifugation may have led to a shift in pH to higher values, thereby enhancing the degree of saturation with respect to carbonate and sulfide minerals. However, an upward shift of ca. 0.5 pH units due to this effect would not greatly affect the observed trends with depth and contrasts between stations in the calculated saturation states presented. Calculated diffusive fluxes of Mn$^{2+}$ vary from 81 to 236 µmol m$^{-2}$ d$^{-1}$, with the highest efflux from the sediment being observed at the hypoxic Bornholm Basin site BY5 and in the anoxic Landsort Deep (LD1)(Table 2).

Average sedimentation rates vary significantly between sites, with 3- to 4-fold higher rates at Fladen and in the Landsort Deep (LD1) when compared to the oxic site in the eastern Gotland Basin (LF1) and Bornholm Basin (BY5)(Table 1; Figure 4). Sediments are highly porous (Appendix B) and rich in organic carbon (TOC) with maxima of ca. 5 wt% at the oxic sites Fladen and LF1 and ca. 16 wt% at the anoxic sites (Figure 4). While changes in TOC with depth at Fladen and LF1 are relatively small, distinct enrichments in TOC are observed in the upper part of the sediment at all anoxic sites. High contents of total Al, which is a proxy for clays, are in line with the presence of fine-grained sediments throughout the cores (Appendix B). Total sulfur contents are low at Fladen, but are higher at all other sites, and show considerable variation with depth in the sediment. Mn is enriched in the surface sediment at Fladen, but is nearly absent at the LF1, BY5 and LF3 sites. At sites LL19, BY15 and F80, Mn is present again but is mostly observed at greater depth in the sediment. The upper 30 cm of the sediment at site LD1 is highly enriched in Mn. Sediment Ca is high at Fladen, is enriched in the surface sediment at site LF1, is low at sites BY5, LF3 and LL19 and follows the pattern in Mn at sites BY15, F80 and LD1. Sediment Fe typically ranges between 2 to 6 wt% and there is a trend towards lower Fe contents in the upper 5 to 20 cm of the sediment, following an initial maximum at the bottom of the TOC-rich interval at many sites (Appendix B). This upward declining trend is even more apparent when the Fe contents are normalized to Al (Figure 4). Sediment Mo is low at the Fladen, LF1, BY5 and LF3 sites but is enriched at the other sites, where profiles largely follow those of TOC (Figure 4).

The LA-ICP-MS line-scans of resin-embedded surface sediments at site LL19 in the Northern Gotland Basin (Figure 5A) support the results of the discrete sample analysis (Figure 4) and

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confirm that there are very few Mn rich laminae in recent sediments at this location. While most of the minor enrichments of Mn are correlated with Fe, S and Mo (Figure 5A), three peaks (at 3.6, 3.9 and 4.6 cm) are independent of these elements, suggesting that these Mn enrichments dominantly consist of carbonates. This is confirmed by the Micro-XRF maps (Figure 5B) of the corresponding interval, which indicate coincident Mn and Ca-rich layers. The maps show clear Mn carbonate layers at ~3.9 cm and ~4.6 cm. However, the third enrichment at 3.6 cm is less continuous and is only represented by one spot in the map. The two distinct Mn carbonate layers can be linked to inflow events in 1993 and 1997, using the $^{210}$Pb-based age model for this site, after correction for compaction of the sediment during embedding.

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In the surface sediments of the Landsort Deep site (LD1), in contrast, a large number of Mn enrichments with much higher concentrations than at LL19 are observed (Figure 4 and 5). The LA-ICP-MS line scans show that highest values often coincide with enrichments in S, Mo and Br but are not related to maxima in Fe. The micro-XRF-maps of Mn, Ca and S confirm that enrichments in Mn are present as discrete layers. The RGB (Mn, Ca, S) composite reveals two different compositions for the Mn enrichments. The purple layers in the RGB composite are a result of enrichments of Mn (red) and S (blue) in the same pixel, suggesting the presence of Mn sulfide. However, other layers and spots are orange to yellow, indicating coincident enrichments of Ca (green) and Mn, suggesting carbonate enrichments (Figure 5B).

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Benthic fluxes of Mn$^{2+}$ and rates of Mn carbonate formation calculated with the diagenetic model depend 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. 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). In runs with low values of $k_{red}$, Mn carbonate is mostly formed in the 2-month anoxic phase. Corresponding profiles of Mn oxides 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. Runs with a higher rate constant for precipitation of Mn carbonates ($k_{prec}$) lead to more sharply defined peaks in Mn carbonate and more Mn carbonate formation at higher $k_{red}$ values, but the same trends in fluxes and rates with varying $k_{red}$ are observed (not shown).

## 4 Discussion

### 4.1 Sediment Mn cycling in the Baltic Sea

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

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

Due to the seasonal and inflow-related changes in redox conditions in the Baltic Sea, the lack of detailed data sets on $Mn^{2+}$ concentrations in the water column, and our very limited number

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**Gelöscht:** , sediments in some shallow areas no longer do so of study sites, we cannot accurately estimate the different reservoirs of Mn and the importance of the present-day source of Mn from sediments overlain by oxic and hypoxic and anoxic bottom waters at the basin scale. Nevertheless, we will attempt to make a rough quantification using the data that is available and will then compare it to estimates from the literature.

Taking an average deep water volume of 2,000 km$^3$ and average hypoxic area of 47,000 km$^2$ (Carstensen et al., 2014) and a deep water concentration of Mn of 8 µM (Löffler et al. 1997 as cited by Heiser et al., 2001), the amount of Mn in the deep water is estimated at 1.6 x 10$^{10}$ mol or 0.33 mol m$^{-2}$. The range in Mn fluxes in our study (0 to 236 µmol m$^{-2}$ d$^{-1}$; Table 2) is comparable to benthic fluxes measured with in-situ chambers in other areas of the Baltic Sea (e.g. the Gulf of Finland; Pakhomova et al., 2007) and estimated from pore water profiles from the 1990's (e.g. Heiser et al., 2001). If we assume that a flux of ca. 90 µmol m$^{-2}$ d$^{-1}$ is representative for the sediments overlain by hypoxic and anoxic bottom waters (Table 2; based on the fluxes for LL19, F80 and BY15), we calculate a yearly flux of 0.033 mol m$^{-2}$ from those sediments, which is equivalent to 10% of the inventory in the water column. In similar calculations, Heiser et al. (2001) estimated the amount of Mn in the Gotland Deep to be equal to 0.8 mol m$^{-2}$. With our estimate of the benthic flux, this would lead to a contribution of the benthic flux of less than 5%.

Note, however, that the role of the benthic flux of Mn from hypoxic sediments will vary spatially and may be biased towards high values because of preferential sampling of sites with a relatively high sediment accumulation rate in most pore water studies. This may explain the one order of magnitude lower benthic fluxes of Mn reported for the Gotland Deep area in 1999-2001 of ca. 7-8 µmol m$^{-2}$ d$^{-1}$ by Neretin et al. (2003) when compared to those in our study (Table 2).

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). The exact impact of inflows on the oxygenation of the bottom waters in the deep basins of the Baltic Sea varies from site to site, however, and depends on the volume and oxygen content of the inflowing water, its pathway and the oxygen concentration in the receiving basin (e.g. Carstensen et al., 2014), with the general flow of water in the deep basins going from the Gotland to the Fårö and the Landsort Deep (Holtermann et al., 2012). For example, the bottom water in the Gotland Deep was free of hydrogen sulfide for 4 months following the inflow of 1993-1994

(Neretin et al., 2003; Yakushev et al., 2011) whereas the Landsort Deep was less affected because the bottom water at the time contained oxygen already (Figure 7). Using biogeochemical modeling of a typical inflow in the Gotland Deep area, Yakushev et al. (2011) showed that dissolved $Mn^{2+}$ in the water column was oxidized to Mn oxides and settled to the bottom over a time period of months. Dissolved $Mn^{2+}$ appeared in the water column again upon the return of bottom water anoxia and steady state conditions in the water column were established in the model after ca. 1.5 years.

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

Notably, Yakushev et al. (2011) consider $Mn^{3+}$ besides $Mn^{2+}$ in their model for biogeochemical dynamics in the water column in the Gotland Deep. Dellwig et al. (2012) found recently that $Mn^{3+}$ is an important component in the water column Mn cycle in the Landsort Deep but not in the Gotland Deep. Further work is required to elucidate the potential importance of this finding to Mn dynamics in the Baltic Sea and its impact on other biogeochemical cycles (e.g. Pakhomova and Yakushev, 2013) and to determine whether $Mn^{3+}$ plays a role in the sediments as well and impacts Mn sequestration (e.g. Madison et al., 2011). Field studies of Mn dynamics in the water column and sediment during and directly after an inflow would be of particular value.

## 4.2 Manganese sequestration in the anoxic basins

Formation of Mn bearing carbonates in the Gotland Basin and Landsort Deep is generally described as being ubiquitous after inflows (e.g. Jakobsen and Postma, 1989). 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

**Gelöscht:** Due to the seasonal and inflow-related changes in redox conditions in the Baltic Sea and our very limited number of study sites, we cannot accurately estimate the importance of the present-day source of Mn from oxic and hypoxic areas at the basin scale. However, we do note that the range in Mn fluxes in our study (0 to 236 µmol $m^{-2}$ $d^{-1}$; Table 2) is comparable to benthic fluxes measured with in-situ chambers in other areas of the Baltic Sea (e.g. the Gulf of Finland; Pakhomova et al., 2007) and estimated from pore water profiles from the 1990's (e.g. Heiser et al., 2001). As discussed by Heiser et al. (2001), an efflux of Mn of this order of magnitude is relatively small compared to the total amount of dissolved Mn in the hypoxic water, which these authors estimate at 0.8 mol $MnO_2$ $m^{-2}$ for an anoxic water column of 100 m in the Gotland Basin. This large pool of Mn in the water column was likely mostly released from the formerly oxic sediments during the initial expansion of hypoxia during the 20th century, and is now only temporarily precipitated again as Mn oxide when the basin becomes oxygenated during inflows (Yakushev et al., 2011). Thus, in contrast to the period of initial expansion of hypoxia, the Mn pool in the water column now depends largely on ambient redox conditions. This is supported by the fact that there is no trend in water column Mn concentrations with time over recent decades (Pohl and Hennings, 2005). We conclude that the present-day Mn shuttle, although active in transporting Mn from the shallow to deep areas, is not as important quantitatively as a source of Mn to the deep basins as it was at the onset of hypoxia early in the 20th century.

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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 $Mn^{2+}$ 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). We observe such enrichments in all our deep basin cores, with the magnitude of the enrichment increasing with water depth (Figure 4). We suggest that this water depth effect between the deep basin sites is due to increased focusing of particulate Mn oxides precipitated during inflow events with water depth, combined with a high alkalinity in the deep basins linked to organic matter degradation by sulfate reduction. Increased focusing of Mn oxides with water depth has been observed in other marine systems (e.g. Slomp et al., 1997) and high alkalinity in sulfate-bearing organic rich sediments overlain by an anoxic water column are typically linked to organic matter degradation through sulfate reduction (Berner et al., 1970).

Our microanalysis results show that the Mn carbonate enrichments at site LL19 are highly laminar in character, implying rapid precipitation at or near the sediment-water interface. Furthermore, these Mn carbonate enrichments occur independently of enrichments in Mo and S. Sedimentary Mo can be used as a proxy for sulfidic conditions close to the sediment-water interface, due to the conversion of seawater oxymolybdate to particle-reactive thiomolybdate in the presence of hydrogen sulfide (Erickson and Helz, 2000). Although the ultimate burial phase of Mo in sulfidic sediments is still debated (e.g., Helz et al., 2011), Mo concentrations have successfully been used to reconstruct the redox history of the bottom water in restricted coastal basins (Adelson et al., 2001; Jilbert and Slomp, 2013a). Sulfur enrichments in sediments are typically associated with Fe-sulfides (Boesen and Postma, 1988), and thus are also indicative of sulfidic conditions close to the sediment-water interface. The independence of Mn enrichments from those of Mo and S suggests relatively oxic conditions at the time of Mn carbonate precipitation. Both lines of evidence support the interpretation of Mn carbonate precipitation following inflow events (Sternbeck and Sohlenius, 1997). Our age model suggests that the two pronounced Mn carbonate layers at the base of the surface-sediment block (Figure 5) correspond to inflows in 1993 and 1997 (Matthäus and Schinke, 1999).

**Gelöscht:** However, strong oversaturation is assumed to be reached following the inflow of oxygenated, saline North Sea water

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Mn enrichments at the Landsort Deep site LD1 occur more frequently when compared to other deep basin sites (Figure 4), as observed in earlier work (Lepland and Stevens, 1998). In the Landsort Deep, Lepland and Stevens (1998) attributed the enrichments to the relatively high alkalinity. Our pore water results show that alkalinity is similar to that of F80. However, the pore water $Mn^{2+}$ concentrations at the Landsort Deep site are much higher than elsewhere (>1 µM versus <0.26 mM of $Mn^{2+}$). This may be related to the fact that the Landsort Deep is the deepest basin in the Baltic Sea and its geometry makes it an excellent sediment trap. As a consequence, sediment deposition rates are much higher than in the other Deeps (Lepland and Stevens, 1998; Mort et al., 2010). Results of the recent IODP expedition suggest that deposition rates may even be more than a factor of 6 higher; (Expedition 347 Scientists, 2014). Sediment focusing is also expected to lead to a higher input of organic matter and Mn oxides to this basin. Given that rates of mineral dissolution are expected to depend on the amount of material present, corresponding rates of input and dissolution of Mn oxide minerals in the sediment are likely higher in the Landsort Deep than at other sites. Thus, we suggest that differences in focusing of the sediment may explain the observed differences in pore water chemistry and Mn sequestration. The differences in pore water chemistry will also likely impact the exact solid phases formed in the sediments of the various deep basins.

The high-resolution analyses for the Landsort Deep site (LD1) also show that, besides Mn carbonate enrichments, there are several distinct layers of Mn sulfide in the surface sediments (Figure 5). These appear to coincide with enrichments in Mo, suggesting formation of Mn sulfides during intervals of more reducing conditions (Mort et al., 2010). Furthermore, we observe simultaneous enrichments of Br (Figure 5), which suggests higher organic carbon contents (Ziegler et al., 2008). 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. We note that the interval presented in the XRF map covers only a few years of sediment accumulation, possibly suggesting rapid changes in Mn mineralogy in response to seasonal variability of the organic matter flux (Figure 5). Primary productivity in the Baltic Sea is known to vary seasonally (Bianchi et al., 2002; Fennel, 1995). Further work is required to determine conclusively the mechanisms of MnS formation. While the presence of MnS has been shown for the earlier anoxic time intervals in the Baltic (Böttcher and Huckriede, 1997; Lepland and Stevens, 1998), this is the first time Mn sulfides are reported for such near-surface sediments in the Baltic Sea.

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**Gelöscht:** This suggests that dissolution of Mn minerals below the surface sediment supplies additional Mn for Mn carbonate formation in the Landsort Deep and allows the more continuous formation. While such a deep sediment pore water source of $Mn^{2+}$ is also observed at the other sites (e.g. LL19 and F80), and may be linked to dissolution of Mn carbonates at greater depth (Heiser et al., 2001; Jilbert and Slomp, 2013), the pore water Mn concentrations are by far the highest at the Landsort Deep site (> 1 mM versus <0.26 mM of $Mn^{2+}$). This "deep" source of Mn may in fact explain why the formation of Mn enrichments is more continuous than at the other sites, rather than the difference in alkalinity as suggested earlier by Lepland and Stevens (1998). We note that the Landsort Deep is the deepest basin in the Baltic Sea and its geometry makes it an excellent sediment trap. As a consequence, sediment deposition rates are much higher than in the other Deeps (Expedition 347 Scientists, 2014; Lepland and Stevens, 1998; Mort et al., 2010), explaining the observed differences in pore water chemistry.

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The contrasting controls on Mn mineral formation in the Landsort Deep, compared to the other deep basin sites, are further illustrated by a comparison of the trends in total Mn and Mo concentrations (Figure 4) with measured bottom water oxygen concentrations for the period 1955 to 2010 (ICES Dataset on Ocean Hydrography 2014) for sites in the northern Gotland Basin (LL19) and the Landsort Deep (LD1) (Figure 7). At site LL19, Mn enrichments in the sediments coincide with low values of Mo in the sediment and inflows of oxygenated water. This suggests that Mn burial is enhanced under more oxygenated bottom water conditions. At LD1, in contrast, high Mn contents are observed from 1965 onwards, independent of inflows, with the highest Mn values coinciding with periods with the highest sulfide concentrations that occur in particular since the year 2000. 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 the other basins.

## 4.3 Changes in Mn burial linked to expanding hypoxia

Strikingly, the more reducing conditions in the Gotland Basin (LL19, BY15) and Fårö Deep sites (F80) over the past decades, as recorded in the Mo profiles (Figures 4 and 7), are accompanied by a strong reduction in sediment Mn burial. Given the suggested link between Mn burial and inflows, it is important to assess the occurrence of these inflows. During the past two decades, there were two major (1993, 2003) and several minor inflow events (e.g. 1997) into the Baltic Sea. The event in 1993 was one of the strongest in the last 60 years (Matthäus et al., 2008) and the inflow of 2003 (Feistel et al., 2003) was weaker but still significant enough to reoxygenate the bottom water of the deep basins (Figure 7). However, at LL19, Mn sequestration in the sediment between 2000 and 2010 has been negligible and the inflow in 2003 is not recorded as a Mn carbonate enrichment (Figure 7), whereas in the high resolution geochemical analyses Mn layers are clearly visible in both the LA-ICP-MS and micro-XRF scans (Figure 5) and can be linked to the inflows in 1993 and 1997. A similar “missing” Mn carbonate layer was observed by Heiser et al. (2001) in the Gotland Deep and attributed to re-dissolution of Mn carbonate linked to resuspension events and mixing of the sediment into unsaturated bottom waters. However, our cores were clearly laminated and the $^{210}$Pb profiles also show no evidence for mixing. We therefore conclude that, with the increased hypoxia and euxinia in the Baltic Sea, Mn oxides are no longer converted to stable Mn carbonates following inflows.

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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 $Mn^{2+}$ concentrations in the surface sediment upon dissolution of Mn oxides following inflows (Lepland and Stevens, 1998). After an inflow, supersaturation with respect to Mn carbonates is thus expected to be reached in the surface sediment and not only at depths below ca. 5-10 cm (Figure 3). But what can inhibit the formation of these Mn carbonates? One possibility is that at high pore water sulfide concentrations, Mn sulfides form instead of Mn carbonates. However, given that there is negligible Mn enrichment in the upper sediments of F80, BY15 and LL19 today, we can exclude that possibility. Mn carbonate formation could be reduced if alkalinity declined, but alkalinity in the bottom waters of the Gotland Deep has in fact increased recently (e.g. Ulfsbo et al., 2011). High phosphate concentrations in the surface sediment may potentially negatively affect the rate of Mn carbonate formation (Mucci, 2004). However, there is no evidence for a significant rise in dissolved phosphate in the pore water of Gotland Basin sediments over the past decades (e.g. Carman and Rahm, 1997; Hille et al., 2005; Jilbert et al., 2011). Alternatively, we hypothesize that the Mn oxides that are formed following modern inflow events might be reductively dissolved faster than previously. As a consequence, the $Mn^{2+}$ released from the oxides could then escape to the overlying water instead of being precipitated in the form of Mn carbonate. This is in line with the results of the simple diagenetic model where high rates of Mn oxide reduction lead to less Mn carbonate formation (Figure 6).

There are multiple possible reductants for Mn oxides in marine sediments, including sulfide, $Fe^{2+}$ (e.g. Canfield and Thamdrup, 2009), $NH_4^+$ (e.g. Luther et al., 1997), and $CH_4$ (Beal et al., 2009), with the role of the latter two reductants in marine sediments still being debated. Given that the $Fe^{2+}$ and $CH_4$ concentrations in the pore waters of the surface sediments of the Gotland Basin area are negligible, these constituents are unlikely to play an important role as a reductant for Mn oxides in the northern Gotland Basin (LL19), Fårö Deep (F80) and Gotland Deep (BY15) sites. Furthermore, there is no evidence for a major recent change in pore water $CH_4$ concentrations in the surface sediments. There is evidence, however, for a recent rise in the bottom water sulfide concentrations in the deep basins of the Baltic Sea (Figure 7) linked to eutrophication (Carstensen et al., 2014). As shown for the northern Gotland Basin site (LL19), the more persistent presence of high concentrations of bottom water sulfide and enrichments in sediment Mo, coincide with the decline in Mn in the sediment (Figure 7).

We hypothesize that Mn oxides that are formed following modern inflow events and that are deposited on the seafloor (Heiser et al., 2001) are no longer being converted to Mn carbonates because of higher ambient concentrations of sulfide in the bottom water and in the pore water. These higher sulfide concentrations are likely the direct result of increased sulfate reduction driven by the ongoing rise in productivity in the Baltic Sea (Gustafsson et al., 2012; Carstensen et al, 2014). The observed decline in Fe/Al at our deep basin sites (Figure 3) suggests more muted shuttling of Fe oxides from shelves to the deeps linked to the expanding hypoxia (e.g. Scholz et al., 2014) which may have reduced the buffer capacity of the sediments for sulfide (e.g. Diaz and Rosenberg, 2008).

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

$$R = kC_{TS}C_{Mnoxides} \qquad (6)$$

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

$$R = k_{red}C_{Mnoxides} \qquad (7)$$

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

**Gelöscht:** We postulate that Mn oxides that are formed following modern inflow events are dissolved much faster than previously because of the more rapid return of sulfide in the surface sediments and the higher sulfide concentrations in the water column linked to the expansion of hypoxia. As a consequence, the $Mn^{2+}$ released from the oxides escapes to the overlying water instead of being precipitated in the form of Mn carbonate. 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 oxides 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 observation suggests that, contrary to suggestions by Scholz et al. (2013), scavenging of Mo by Mn (oxyhydr)oxides is not at present a major vector for Mo delivery to the sediment surface in the Gotland Deep.

### 4.4 Implications for Mn as a redox proxy

In the classic model of Calvert and Pedersen (1993), Mn enrichments in sediments are indicative of either permanent or temporary oxygenation of bottom waters. Sediments of permanently anoxic basins, in contrast, are assumed to have no authigenic Mn enrichments because there is no effective mechanism to concentrate the Mn oxides. Our results for the Gotland Deep area indicate that the temporary oxygenation of the basin linked to inflows is no longer recorded as a Mn enrichment in the recent sediment when hypoxia becomes basin-wide. Thus, a decline in Mn burial (or a complete lack of Mn) in geological deposits in combination with indicators for water column euxinia such as elevated Mo contents may point towards expanding hypoxia, but does not exclude temporary oxygenation events. Strikingly, only very little Mn was buried at sites F80 and LL19 during the previous period of hypoxia in the Baltic Sea during the Medieval Climate Anomaly (Jilbert and Slomp, 2013b) as well as at the end of the Holocene Thermal Maximum at site LL19 (Lenz et al., 2014). This may be in line with hypoxia that was equally intense and widespread in the basin at the time as it is today. Our results for the Landsort Deep suggests that Mn enrichments may also form frequently in an anoxic basin as Mn carbonates and sulfides if the input of Mn from the surrounding area is exceptionally high due to sediment focusing. Mn enrichments in geological deposits thus can be indicative of both oxic and anoxic depositional environments, emphasizing the need for multiple redox proxies.

**Gelöscht:** indicate

**Gelöscht:** if there is a deep pore water source of dissolved $Mn^{2+}$. Such a deep source is expected to be important at sites where abundant Mn has accumulated during previous periods of more oxic conditions

## 5 Conclusions

We show that the most recent sediments in the Fårö Deep and Gotland Deep contain low concentrations of Mn near the sediment surface. We hypothesize that this is due to the expansion of the area with hypoxic bottom waters and the development of more continuous bottom water euxinia over the past decades, linked to ongoing eutrophication and possibly due to the reduced input of Fe-oxides that can act as a sink for sulfide. The high ambient sulfide concentrations in the sediment and water column after an inflow event are suggested to contribute to conditions that are conducive to faster dissolution of Mn oxides, leading to less formation of Mn carbonates and more loss of $Mn^{2+}$ to the water column. Our hypothesis is supported by the results of a simple diagenetic model for Mn. It is also in accordance 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). In the Landsort Deep, in contrast,

**Gelöscht:** Our work demonstrates that the efflux of Mn from sediments in the Baltic Sea is relatively small compared to the existing reservoir of Mn in the anoxic deep waters. Although abundant dissolved Mn is available in the water column, Mn-enrichments are no longer forming in all of the anoxic basins of the central Baltic Sea.

**Gelöscht:** postulate

**Gelöscht:** hypoxia

**Gelöscht:** with the Mn oxides formed during inflows from the North Sea often being reduced so rapidly that the $Mn^{2+}$ is lost to the water column.

Mn sulfides and carbonates are still being precipitated. This could be due to strong focusing of Mn rich sediment particles and high rates of sediment accumulation in the Landsort Deep. Our results indicate that sediment Mn carbonates in the other deep basins of Baltic Sea no longer reliably and consistently record inflows of oxygenated North Sea water. This has implications for the use of Mn enrichments as a redox proxy when analyzing geological deposits.

**Gelöscht:** This is attributed to an additional diffusional source of Mn from deeper pore water

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**Gelöscht:** -NWO

**Gelöscht:** Bo Gustafsson is thanked for providing water column data.

## References

Adelson, J. M., Helz, G. R., and Miller, C. V.: Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake Bay sediments, Geochim Cosmochim Acta, 65, 237-252, 2001.

Ahl, T.: River Discharges of Fe, Mn, Cu, Zn, and Pb into the Baltic Sea from Sweden, Ambio Special Report, 219-228, 1977.

Appleby, P. and Oldfield, F.: The assessment of $^{210}$Pb data from sites with varying sediment accumulation rates, Hydrobiology, 103, 29-35, 1983.

Beal, E. J., House, C. H., and Orphan, V. J.: Manganese- and Iron-Dependent Marine Methane Oxidation, Science, 325, 184-187, 2009.

Berner, R. A.: Early diagenesis: A theoretical approach, Princeton University Press, 1980.

Berner, R. A., Scott, M. R. and Thomlinson, C.: Carbonate alkalinity in the pore waters of anoxic marine sediments, Limno. Oceanogr. 15(4), 544-549, 1970.

Bianchi, T. S., Rolff, C., Widbom, B., and Elmgren, R.: Phytoplankton Pigments in Baltic Sea Seston and Sediments: Seasonal Variability, Fluxes, and Transformations, Estuar Coast Shelf Sci, 55, 369-383, 2002.

Boesen, C. and Postma, D.: Pyrite formation in anoxic environments of the Baltic, Am J Sci, 288, 575-603, 1988.

Böttcher, M. E. and Huckriede, H.: First occurrence and stable isotope composition of authigenic γ-MnS in the central Gotland Deep (Baltic Sea), Mar Geol, 137, 201-205, 1997.

Boudreau, B. P.: Diagenetic models and their implementation: modelling transport and reactions in aquatic sediments, Springer Berlin, 1997.

Cai, W.-J and Reiners, C. E.: The development of pH and $pCO_2$ microelectrodes for studying the carbonate chemistry of pore waters near the sediment-water interface, Limnol. Oceanogr., 38(8), 1762-1773, 1993.

Calvert, S. and Pedersen, T.: Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological record, Mar Geol, 113, 67-88, 1993.

Calvert, S. and Pedersen, T.: Sedimentary geochemistry of manganese; implications for the environment of formation of manganiferous black shales, Econ Geol, 91, 36-47, 1996.

Canfield, D. E. and Thamdrup, B.: Towards a consistent classification scheme for geochemical environments, or, why we wish the term 'suboxic' would go away, Geobiology, 7, 385-392, 2009.

Carman, R. and Rahm, L.: Early diagenesis and chemical characteristics of interstitial water and sediments in the deep deposition bottoms of the Baltic proper, J Sea Res, 37, 25-47, 1997.

Carstensen, J., Andersen, J. H., Gustafsson, B. G., and Conley, D. J.: Deoxygenation of the Baltic Sea during the last century, PNAS 111, 5628-5633, 2014.

Conley, D. J., Björck, S., Bonsdorff, E., Carstensen, J., Destouni, G., Gustafsson, B. G., Hietanen, S., Kortekaas, M., Kuosa, H., Meier, H. E., Müller-Karulis, B., Nordberg, K., Norkko, A., Nürnberg, G., Pitkänen, H., Rabalais, N. N., Rosenberg, R., Savchuk, O. P., Slomp, C. P., Voss, M., Wulff, F., and Zillen, L.: Hypoxia-related processes in the Baltic Sea, Environ Sci Technol, 43, 3412-3420, 2009.

Dellwig, O., Leipe, T., März, C., Glockzin, M., Pollehne, F., Schnetger, B., Yakushev, E. V., Böttcher, M. E., and Brumsack, H.-J.: A new particulate Mn–Fe–P-shuttle at the redoxcline of anoxic basins, Geochim Cosmochim Acta, 74, 7100-7115, 2010.

Dellwig, O., Schnetger, B., Brumsack, H.-J., Grossart, H.-P., and Umlauf, L.: Dissolved reactive manganese at pelagic redoxclines (part II): Hydrodynamic conditions for accumulation, J Mar Syst, 90, 31-41, 2012.

Diaz, R. J. and Rosenberg, R.: Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna, Oceanography and marine biology. An annual review, 33, 245-203, 1995.

Emerson, S., Jacobs, L., and Tebo, B.: The Behavior of Trace Metals in Marine Anoxic Waters: Solubilities at the Oxygen-Hydrogen Sulfide Interface. In: Trace Metals in Sea Water, Wong, C. S., Boyle, E., Bruland, K., Burton, J. D., and Goldberg, E. (Eds.), NATO Conference Series, Springer US, 1983.

Erickson, B. E. and Helz, G. R.: Molybdenum(VI) speciation in sulfidic waters: Stability and lability of thiomolybdates, Geochim Cosmochim Acta, 64, 1149-1158, 2000.

Expedition 347 Scientists: Baltic Sea Basin Paleoenvironment: paleoenvironmental evolution of the Baltic Sea Basin through the last glacial cycle. *IODP Prel. Rept.*, 347, 2014. doi:10.2204/iodp.pr.347.2014

Feistel, R., Nausch, G., Mohrholz, V., Lysiak-Pastuszak, E., Seifert, T., Matthaus, W., Kruger, S., and Hansen, I. S.: Warm waters of summer 2002 in the deep Baltic Proper, Oceanologia, 45, 571-592, 2003.

Fennel, W.: A model of the yearly cycle of nutrients and plankton in the Baltic Sea, J Mar Syst, 6, 313-329, 1995.

Fonselius, S. and Valderrama, J.: One hundred years of hydrographic measurements in the Baltic Sea, J Sea Res, 49, 229-241, 2003.

Gustafsson, B. G., Schenk, F., Blenckner, T., Eilola, K., Meier, H. M., Müller-Karulis, B., Neumann, T., Ruoho-Airola, T., Savchuk, O. P., and Zorita, E.: Reconstructing the development of Baltic Sea eutrophication 1850–2006, Ambio, 41, 534-548, 2012.

Heiser, U., Neumann, T., Scholten, J., and Stüben, D.: Recycling of manganese from anoxic sediments in stagnant basins by seawater inflow: A study of surface sediments from the Gotland Basin, Baltic Sea, Mar Geol, 177, 151-166, 2001.

Helz, G. R., Bura-Nakić, E., Mikac, N., and Ciglenečki, I.: New model for molybdenum behavior in euxinic waters, Chem Geol, 284, 323-332, 2011.

Hille, S., Nausch, G., and Leipe, T.: Sedimentary deposition and reflux of phosphorus (P) in the Eastern Gotland Basin and their coupling with P concentrations in the water column, Oceanologia, 47, 663-679, 2005.

Holtermann, P. L. and Umlauf, L.: The Baltic Sea Tracer Release Experiment: 2. Mixing processes, Journal of Geophysical Research: Oceans, 117, C01022, 2012.

Huckriede, H. and Meischner, D.: Origin and environment of manganese-rich sediments within black-shale basins, Geochim Cosmochim Acta, 60, 1399-1413, 1996.

Huerta-Diaz, M. A. and Morse, J. W.: Pyritization of trace metals in anoxic marine sediments, Geochim Cosmochim Acta, 56, 2681-2702, 1992.

ICES Dataset on Ocean Hydrography. The International Council for the Exploration of the Sea, Copenhagen. 2014.

Jacobs, L., Emerson, S., and Skei, J.: Partitioning and transport of metals across the O2/H2S interface in a permanently anoxic basin: Framvaren Fjord, Norway, Geochim Cosmochim Acta, 49, 1433-1444, 1985.

**Gelöscht:** Gustafsson, B. G. and Medina, M. R.: Validation data set compiled from Baltic Environmental Database. Version 2: Stockholm University Baltic Nest Institute Technical Report 2, 25 p., 2011.¶

Jakobsen, R. and Postma, D.: Formation and solid solution behavior of Ca-rhodochrosites in marine muds of the Baltic deeps, Geochim Cosmochim Acta, 53, 2639-2648, 1989.

Jilbert, T. and Slomp, C. P.: Iron and manganese shuttles control the formation of authigenic phosphorus minerals in the euxinic basins of the Baltic Sea, Geochim Cosmochim Acta, 107, 155-169, 2013a.

Jilbert, T. and Slomp, C. P.: Rapid high-amplitude variability in Baltic Sea hypoxia during the Holocene, Geology, 41, 1183-1186, 2013b.

Jilbert, T., Slomp, C. P., Gustafsson, B. G., and Boer, W.: Beyond the Fe-P-redox connection: preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles, Biogeosciences, 8, 1699-1720, 2011.

Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D. E., Stracke, A., Birbaum, K., and Frick, D. A.: Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines, Geostand Geoanal Res, 35, 397-429, 2011.

Jones, C., Crowe, S. A., Sturm, A., Leslie, K., MacLean, L., Katsev, S., Henny, C., Fowle, D. A., and Canfield, D. E.: Biogeochemistry of manganese in ferruginous Lake Matano, Indonesia, Biogeosciences, 8, 2977-2991, 2011.

Katsikopoulos, D., Fernández-González, A. and Prieto, M.: Precipitation and mixing properties of the “disordered” (Mn,Ca)CO3 solid solution, Geochim Cosmochim Acta 73, 6147-6161, 2009.

Kulik, D. A., Kersten, M., Heiser, U. and Neumann, T.: Application of Gibbs Energy Minimization to Model Early-Diagenetic Solid-Solution Aqueous-Solution Equilibria Involving Authigenic Rhodochrosites in Anoxic Baltic Sea Sediments, Aquatic Geochemistry 6, 147-199, 2000.

Lenz, C., Behrends, T., Jilbert, T., Silveira, M., and Slomp, C. P.: Redox-dependent changes in manganese speciation in Baltic Sea sediments from the Holocene Thermal Maximum: An EXAFS, XANES and LA-ICP-MS study, Chem Geol, 370, 49-57, 2014.

Lepland, A. and Stevens, R. L.: Manganese authigenesis in the Landsort Deep, Baltic Sea, Mar Geol, 151, 1-25, 1998.

**Gelöscht:** Jilbert, T. and Slomp, C. P.: Rapid high-amplitude variability in Baltic Sea hypoxia during the Holocene, Geology, doi: 10.1130/g34804.1, 2013.

Löffler, A.: The importance of particles for the distribution of trace metals in the Baltic Sea, especially under changing redox conditions in the central Baltic deep basins., Meereswissenschaftliche Berichte Warnemünde, 27, 153, 1997.

Luther III, G. W., Rickard, D. T., Theberge, S., and Olroyd, A.: Determination of metal (bi) sulfide stability constants of Mn2+, Fe2+, Co2+, Ni2+, Cu2+, and Zn2+ by voltammetric methods, Environ Sci Technol, 30, 671-679, 1996.

Luther III, G. W., Sundby, B., Lewis, B. L., Brendel, P. J., and Silverberg, N.: Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen, Geochim Cosmochim Acta, 61, 4043-4052, 1997.

Lyons, T. W. and Severmann, S.: A critical look at iron paleoredox proxies: New insights from modern euxinic marine basins, Geochim Cosmochim Acta, 70, 5698-5722, 2006.

MacDonald, R. W. and Gobeil, C.: Manganese sources and sinks in the Arctic Ocean with reference to periodic enrichments in basin sediments, Aquat Geochem, 18, 565-591, 2012.

Madison, A. S., Tebo, B. M., and Luther, G. W.: Simultaneous determination of soluble manganese (III), manganese (II) and total manganese in natural (pore) waters, Talanta, 84, 374-381, 2011.

Manheim, F. T.: A geochemical profile in the Baltic Sea, Geochim Cosmochim Acta, 25, 52-70, 1961.

Martin, J.-M. and Meybeck, M.: Elemental mass-balance of material carried by major world rivers, Mar Chem, 7, 173-206, 1979.

Matthäus, W. and Schinke, H.: The influence of river runoff on deep water conditions of the Baltic Sea, Hydrobiologia, 393, 1-10, 1999.

Matthäus, W. and Franck, H.: Characteristics of major Baltic inflows--a statistical analysis, Cont Shelf Res, 12, 1375-1400, 1992.

Matthäus, W., Nehring, D., Feistel, R., Nausch, G., Mohrholz, V., and Lass, H.-U.: The Inflow of Highly Saline Water into the Baltic Sea. In: State and Evolution of the Baltic Sea, 1952–2005, John Wiley & Sons, Inc., 2008.

Meister, P., Bernasconi, S. M., Aiello, I. W., Vasconcelos, C., and McKenzie, J. A.: Depth and controls of Ca-rhodochrosite precipitation in bioturbated sediments of the Eastern

Equatorial Pacific, ODP Leg 201, Site 1226 and DSDP Leg 68, Site 503, Sedimentology, 56, 1552-1568, 2009.

Mort, H. P., Slomp, C. P., Gustafsson, B. G., and Andersen, T. J.: Phosphorus recycling and burial in Baltic Sea sediments with contrasting redox conditions, Geochim Cosmochim Acta, 74, 1350-1362, 2010.

**Gelöscht:** Mercone, D., Thomson, J., Abu-Zied, R., Croudace, I., and Rohling, E.: High-resolution geochemical and micropalaeontological profiling of the most recent eastern Mediterranean sapropel, Mar Geol, 177, 25-44, 2001.¶

Mouret, A., Anschutz, P., Lecroart, P., Chaillou, G., Hyacinthe, C., Deborde, J., Jorissen, F., Deflandre, B., Schmidt, S., and Jouanneau, J.-M.: Benthic geochemistry of manganese in the Bay of Biscay, and sediment mass accumulation rate, Geo-Mar Lett, 29, 133-149, 2009.

Mucci, A.: The behavior of mixed Ca–Mn carbonates in water and seawater: controls of manganese concentrations in marine porewaters, Aquat Geochem, 10, 139-169, 2004.

Neretin, L. N., Pohl, C., Jost, G., Leipe, T., and Pollehne, F.: Manganese cycling in the Gotland Deep, Baltic Sea, Mar Chem, 82, 125-143, 2003.

Neumann, T., Christiansen, C., Clasen, S., Emeis, K.-C., and Kunzendorf, H.: Geochemical records of salt-water inflows into the deep basins of the Baltic Sea, Cont Shelf Res, 17, 95-115, 1997.

Neumann, T., Heiser, U., Leosson, M. A., and Kersten, M.: Early diagenetic processes during Mn-carbonate formation: Evidence from the isotopic composition of authigenic Ca-rhodochrosites of the Baltic Sea, Geochim Cosmochim Acta, 66, 867-879, 2002.

Pakhomova, S. and Yakushev, E. V.: Manganese and Iron at the Redox Interfaces in the Black Sea, the Baltic Sea, and the Oslo Fjord. In: Chemical Structure of Pelagic Redox Interfaces, Yakushev, E. V. (Ed.), The Handbook of Environmental Chemistry, Springer Berlin Heidelberg, 2013.

Pakhomova, S. V., Hall, P. O., Kononets, M. Y., Rozanov, A. G., Tengberg, A., and Vershinin, A. V.: Fluxes of iron and manganese across the sediment–water interface under various redox conditions, Mar Chem, 107, 319-331, 2007.

Parkhurst, D. L. and Appelo, C.: User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, US Geological Survey Water-Resources Investigations Report 99-4259, 312 pp., 1999.

Passier, H. F., Böttcher, M. E., and de Lange, G. J.: Sulphur enrichment in organic matter of eastern mediterranean sapropels: A study of sulphur isotope partitioning, Aquat Geochem, 5, 99-118, 1999.

Pohl, C. and Hennings, U.: The coupling of long-term trace metal trends to internal trace metal fluxes at the oxic–anoxic interface in the Gotland Basin (57° 19, 20′ N; 20° 03, 00′ E) Baltic Sea, J Mar Syst, 56, 207-225, 2005.

Rickard, D.: The solubility of FeS, Geochim Cosmochim Acta, 70, 5779-5789, 2006.

Riley, J. P.: The Spectrophotometric Determination of Ammonia in Natural Waters with Particular Reference to Sea-Water, Anal Chim Acta, 9, 575-589, 1953.

Savchuk, O. P., Wulff, F., Hille, S., Humborg, C., and Pollehne, F.: The Baltic Sea a century ago—a reconstruction from model simulations, verified by observations, J Mar Syst, 74, 485-494, 2008.

Scholz, F., McManus, J., and Sommer, S.: The manganese and iron shuttle in a modern euxinic basin and implications for molybdenum cycling at euxinic ocean margins, Chem Geol, 355, 56-68, 2013.

Scholz, F., McManus, J., Mix, A. C., Hensen, C., and Schneider, R. R.: The impact of ocean deoxygenation on iron release from continental margin sediments, Nat. Geosci., 7, 433-437, 2014.

Slomp, C. P., Malschaert, J. F. P., Lohse, L., and Van Raaphorst, W.: Iron and manganese cycling in different sedimentary environments on the North Sea continental margin, Cont Shelf Res, 17, 1083-1117, 1997.

Soetaert, K., Petzoldt, T., and Meysman, F.: Marelac: Tools for aquatic sciences. R Package Version 2.1.3. 2010.

Soetaert, K. and Meysman, F.: Reactive transport in aquatic ecosystems: Rapid model prototyping in the open source software R, Environmental Modelling & Software, 32, 49-60, 2012.

Sternbeck, J. and Sohlenius, G.: Authigenic sulfide and carbonate mineral formation in Holocene sediments of the Baltic Sea, Chem Geol, 135, 55-73, 1997.

Strickland, J. D. H. and Parsons, T. R.: A practical handbook of seawater analysis, Fisheries Research Board of Canada, Ottawa, Canada, 1972.

Suess, E.: Mineral phases formed in anoxic sediments by microbial decomposition of organic matter, Geochim Cosmochim Acta, 43, 339-352, 1979.

Sundby, B., Silverberg, N., and Chesselet, R.: Pathways of manganese in an open estuarine system, Geochim Cosmochim Acta, 45, 293-307, 1981.

Turnewitsch, R. and Pohl, C.: An estimate of the efficiency of the iron-and manganese-driven dissolved inorganic phosphorus trap at an oxic/euxinic water column redoxcline, Global Biogeochem Cycles, 24, GB4025, 2010.

Ulfsbo, A., Hulth, S., and Anderson, L. G.: pH and biogeochemical processes in the Gotland Basin of the Baltic Sea, Mar Chem, 127, 20-30, 2011.

van Santvoort, P. J. M., De Lange, G. J., Thomson, J., Colley, S., Meysman, F. J. R., and Slomp, C. P.: Oxidation and origin of organic matter in surficial eastern mediterranean hemipelagic sediments, Aquat Geochem, 8, 153-175, 2002.

Wang, Y. and Van Cappellen, P.: A multicomponent reactive transport model of early diagenesis: Application to redox cycling in coastal marine sediments, Geochim Cosmochim Acta, 60, 2993-3014, 1996.

Yakushev, E. V., Kuznetsov, I. S., Podymov, O. I., Burchard, H., Neumann, T., and Pollehne, F.: Modeling the influence of oxygenated inflows on the biogeochemical structure of the Gotland Sea, central Baltic Sea: Changes in the distribution of manganese, Comput Geosci, 37, 398-409, 2011.

Yeats, P., Sundby, B., and Bewers, J.: Manganese recycling in coastal waters, Mar Chem, 8, 43-55, 1979.

Ziegler, M., Jilbert, T., de Lange, G. J., Lourens, L. J., and Reichart, G. J.: Bromine counts from XRF scanning as an estimate of the marine organic carbon content of sediment cores, Geochem Geophy Geosy, 9, Q05009, 2008.

Zillén, L., Lenz, C., and Jilbert, T.: Stable lead (Pb) isotopes and concentrations – A useful independent dating tool for Baltic Sea sediments, Quat Geochronol, 8, 41-45, 2012.

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

| **Site name** | **Location** | **Cruise** | **Position** | **Water depth (m)** | **Sedimentation Rate (cm yr$^{-1}$)** | **Redox** | **Salinity** |
|---|---|---|---|---|---|---|---|
| Fladen | Fladen | R/V Skagerak<br>Sept. 2007 | 57°11.57N<br>11°39.25E | 82 | 1.0 | oxic | 34.2 |
| LF1 | Northern Gotland Basin | R/V Aranda<br>May/June 2009 | 57°58.95N<br>21°16.84E | 67 | 0.25 | oxic | 8.2 |
| BY5 | Bornholm Basin | R/V Skagerak<br>Sept. 2007 | 55°15.16N<br>15°59.16E | 89 | 0.23 | $O_2$=4.0 µM | 16.2 |
| LF3 | Eastern Gotland Basin | Sediment:<br>R/V Aranda<br>May/June 2009<br>Pore water:<br>R/V Pelagia<br>May 2011 | 57°59.50N<br>20°46.00E | 95 | 0.50 | $H_2S$=2.9 µM | 10.1 |
| LL19 | Northern Gotland Basin | Sediment:<br>R/V Aranda<br>May/June 2009<br>Pore water:<br>R/V Heincke<br>July 2010 | 58°52.84N<br>20°18.65E | 169 | 0.30 | $H_2S$=19.9 µM | 11.4 |
| BY15 | Gotland Deep | Sediment<br>R/V Aranda<br>May/June 2009<br>Pore water: | 57°19.20N<br>20°03.00E | 238 | 0.27 | $H_2S$=74.1 µM | 12.5 |

**Gelöscht:** Negative $O_2$ values indicate the presence of $H_2S$ assuming that 1 mol of $H_2S$ is equivalent to 2 mol $O_2$.

**Gelöscht:** 0.09

**Gelöscht:** mLL$^{-1}$

**Gelöscht:** O

**Gelöscht:** -0.13

**Gelöscht:** mLL$^{-1}$

**Gelöscht:** O

**Gelöscht:** -0.89

**Gelöscht:** mLL$^{-1}$

**Gelöscht:** O

**Gelöscht:** -3.32

**Gelöscht:** mLL$^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | R/V Heincke<br>July 2010 | | | | | |
| F80 | Fårö Deep | Sediment:<br>R/V Aranda<br>May/June 2009<br>Pore water:<br>R/V Heincke<br>July 2010 | 58°00.00N<br>19°53.81E | 191 | 0.55 | $H_2S$=45.6 µM | 12.0 |
| LD1 | Landsort Deep | R/V Pelagia May 2011 | 58°37.47N<br>18°15.23E | 416 | 0.77 | anoxic and sulfidic | 10.6 |

**Gelöscht:** O

**Gelöscht:** -2.04

**Gelöscht:** mLL$^{-1}$

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

| Site | Location | Year and cruise | Depth range<br>cm | Diffusive Mn flux<br>µmol $m^{-2}$ $d^{-1}$ |
|---|---|---|---|---|
| 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 |

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

**Gelöscht:** 8

**Gelöscht:** LF3 ... [1]

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

| **Environmental and transport Parameters** | **Value** | **Source** |
|---|---|---|
| - Porosity (vol%) | 99 | Appendix B |
| - Temperature (ºC) | 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 $MnCO_3$ (mol $m^{-2}$ $y^{-1}$) | 0 | Assuming all formation in the sediment |
| Transient flux of Mn oxides (mol $m^{-2}$ $y^{-1}$) | 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 |

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

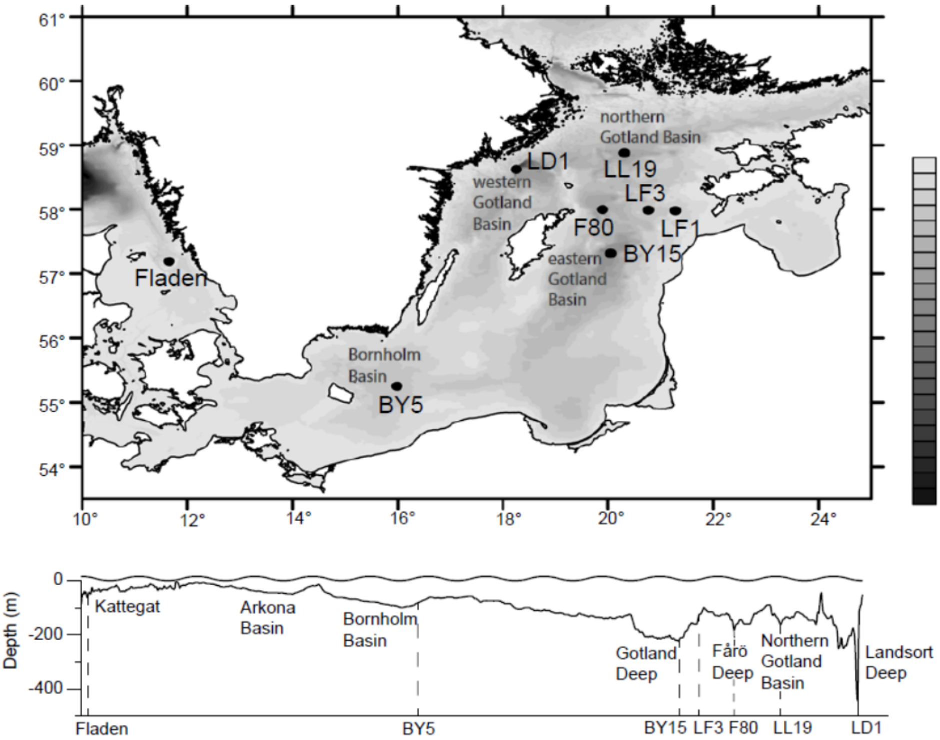

Figure 1 Bathymetric map and depth profile of the Baltic Sea showing the locations of the sampling sites.

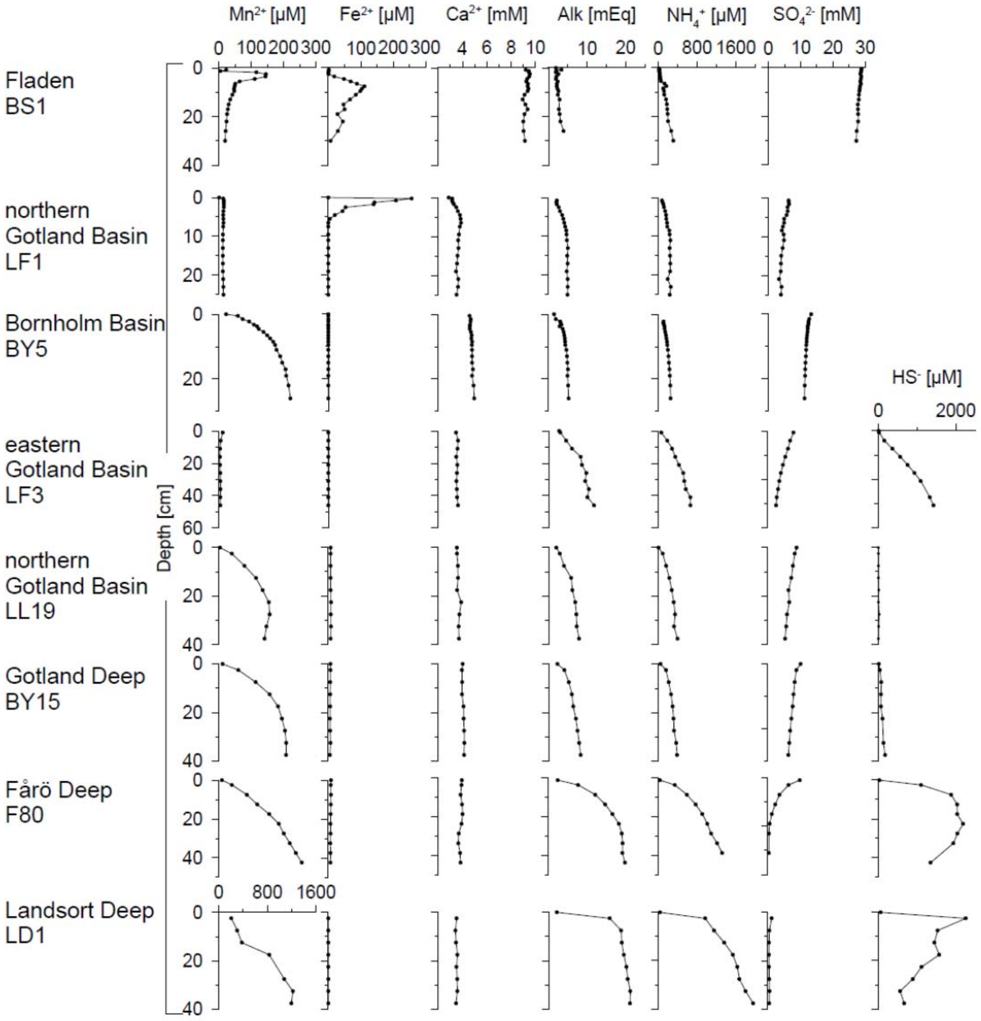

Figure 2 Pore water profiles of manganese (II), iron (Fe), calcium, alkalinity, ammonium and sulfate for all 8 sites and hydrogen sulfide for the 5 deepest sites. Note, that $Fe^{2+}$ is below detection limit in core LF3 and LD1 and dissolved sulfide is expressed as $HS^-$, some $H_2S$ can be present as well.

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**Gelöscht:** here

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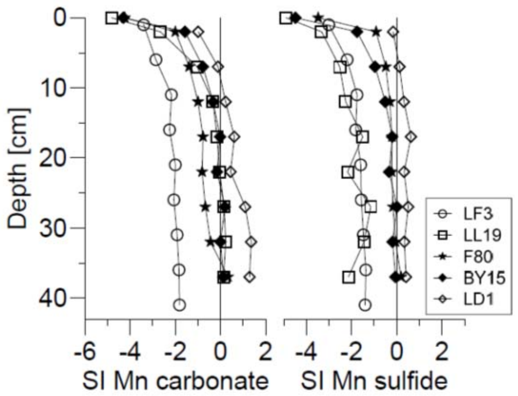

Figure 3 Saturation indices (SI) for Mn carbonate (here as $Mn_{0.74}Ca_{0.26}CO_3$) and Mn sulfide as calculated from the pore water data with PHREEQC.

**Gelöscht:** S

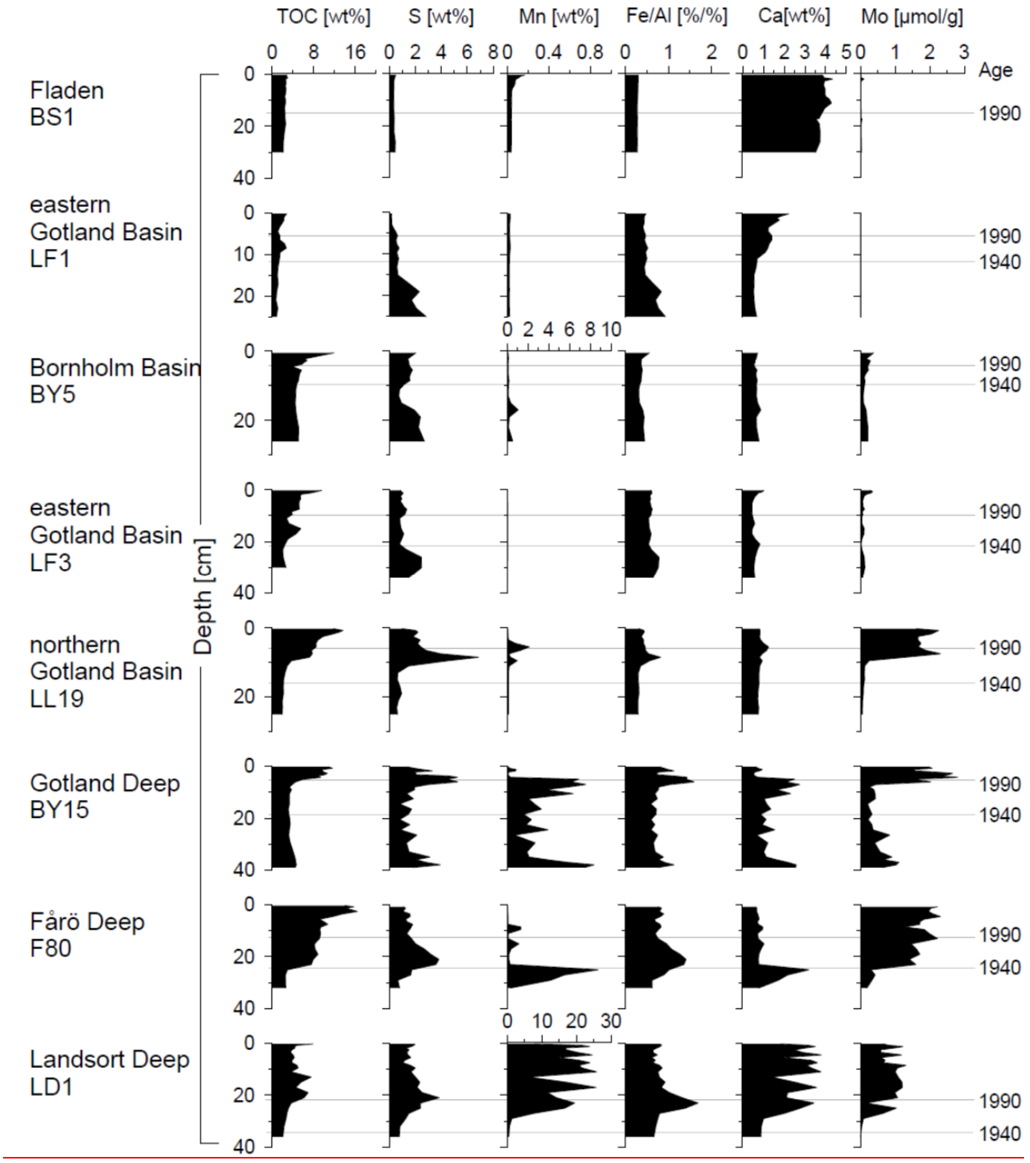

Figure 4 Sediment depth profiles of total organic carbon (TOC), sulfur (S), manganese (Mn), iron to aluminum ratio (Fe/Al), calcium (Ca) and molybdenum for all 8 sites. Note the different scale for manganese at Fladen and LF1, and LD1. Grey lines indicate the years 1990 and 1940, based on sediment dating.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

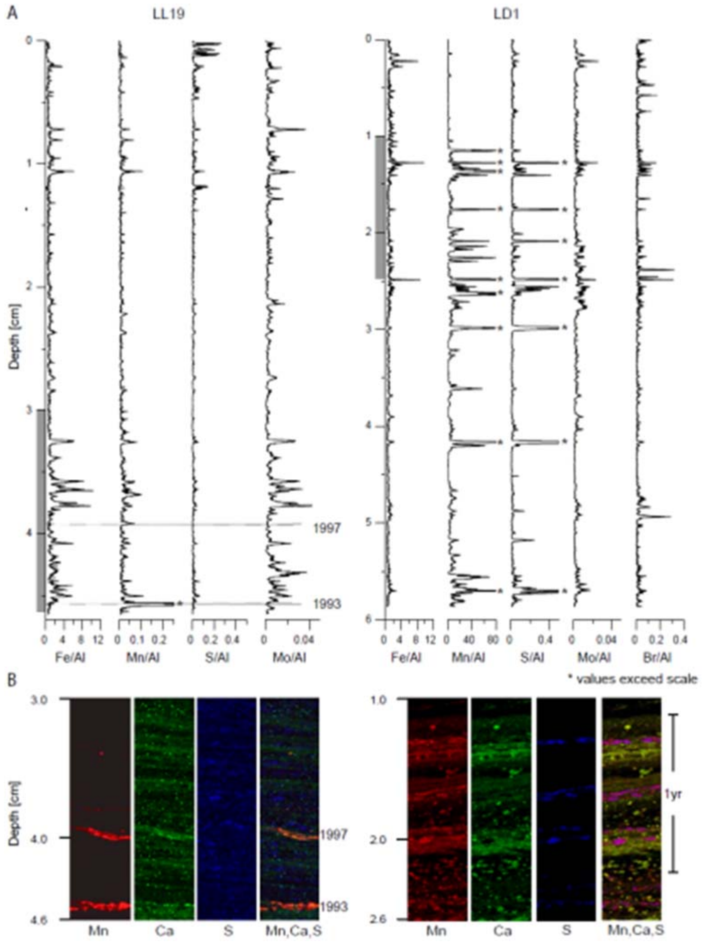

Figure 5 A: High resolution elemental profiles of Fe/Al, Mn/Al, S/Al, Mo/Al and Br/Al (only LD1) generated by LA-ICP-MS line scanning for resin-embedded surface sediment blocks. Note the difference in absolute values for Mn/Al between LL19 and LD1. The depth scale refers to the compacted sediment in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

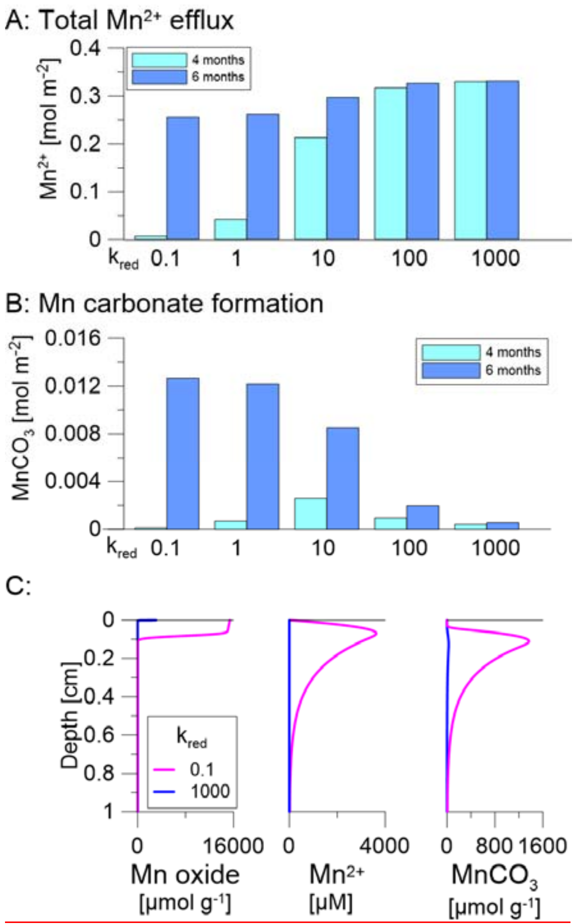

Figure 6. A: Total sediment-water exchange of $Mn^{2+}$ and B: integrated rates of Mn carbonate formation over the upper cm of the sediment (in mol $m^{-2}$) for the first 4 months (with $k_{red}$ either 0.1, 1, 10, 100 or 1000 $yr^{-1}$) and for the total 6 months (with $k_{red}$ equal to 1000 $yr^{-1}$ to represent anoxia during the last two months of each simulation) as described in the text. C: Depth profiles of Mn oxide (after 4 months), $Mn^{2+}$ at the start of the anoxic phase and $MnCO_3$ (after 6 months) as calculated with the model in the same scenarios as A and B.

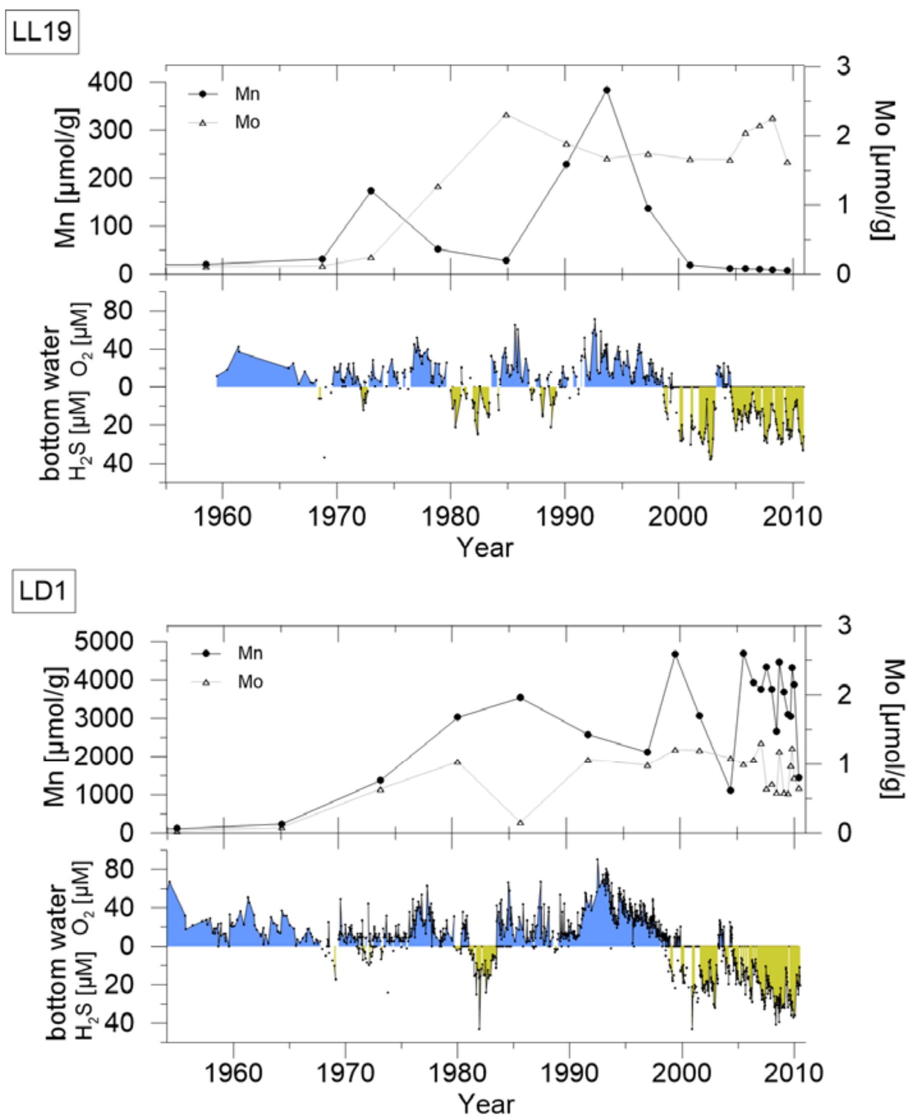

Figure 7 Records of sediment manganese and molybdenum for 1955-2010 for core LL19 and core LD1 and corresponding bottom water oxygen and sulfide concentrations from monitoring data (for LD1 the nearby monitoring station LL23 was used; ICES Dataset on Ocean Hydrography, 2014).

**Gelöscht:** 6

**Gelöscht:** Baltic Sea Environmental Database at Stockholm University; http://nest.su.se/bed/ACKNOWLE.shtml

**Gelöscht:** Negative $O_2$ values indicate the presence of $H_2S$ assuming that 1 mol $H_2S$ is equivalent to 2 mol $O_2$.