Biogeosciences
Discussions

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Interactive comment on "Are recent changes in sediment manganese sequestration in the euxinic basins of the Baltic Sea linked to the expansion of hypoxia?" *by* C. Lenz et al.

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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.

reviewer comment:

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.

Answer:

Here, we are not referring to the benthic release fluxes, i.e. the sediment-water exchange of Mn2+ as presented in Table 2. Instead, we are discussing the diffusive source of Mn from deeper sediment layers towards the surface sediment. That deeper source is much greater at the Landsort Deep site than at the other sites. While we do not explicitly calculate that flux, Figure 5 shows that Mn2+ concentrations at depth at the Landsort Deep site are far greater than at the other sites (> 1 mM at LD1 versus ca. 0.2 mM at F80). Regarding the bottom water value for LD1 in the flux calculations: see our response to reviewer #1.

We have now modified the corresponding text to make it clearer that we are not referring to the benthic flux and instead are referring to diffusion from deeper in the sediment to the surface sediments (page 9902 from line 12 to 21): "However, the pore water Mn2+ concentrations at depth in the sediment at the Landsort Deep site are much higher than elsewhere. 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 in the surface sediment. While such a deep sediment pore water source of Mn2+ 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 Mn2+). 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, rather

than the difference in alkalinity as suggested earlier by Lepland and Stevens (1998)."

reviewer comment:

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.

Answer:

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 a section on page 9902 (line 21) providing a few more details on

the depositional environment in the Landsort Deep and how it differs from the other basins. "Note that the Landsort Deep is the deepest basin 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."

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)."

reviewer comment:

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.

Answer:

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 we accept that frequency of inflows (which has indeed declined since 1980) is one factor playing 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. 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 a few lines in the text of 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 [. . .]."

reviewer comment:

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.

Answer:

Water column records for the deep basins for the last decade indicate permanently euxinic conditions in the water column (Figure 6; e.g. data bases SMHI) since the last major inflow in 2003. Mn oxides do not survive vertical transport though highly sulfidic waters and thus are not expected to reach the sediment during such periods. (see

Dellwig et al., 2010). Our sediment records (e.g. LL19 and F80 in Figure 4) show the abundant presence of Mo in the sediment even during such periods of permanent euxinia. We thus conclude that the Mn shuttle cannot be important for Mo transfer to the sediment in the deep basins at present.

We have now extended the text on page 9904 to make this clearer.

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

reviewer comment:

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).

Answer:

We refer the reviewer to Figure 4 in the paper by Jilbert and Slomp (2013; Geology).

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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 Corg/P in these sediments, as presented in the same paper.

reviewer comment:

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.

Answer:

We agree that a deep source of dissolved Mn2+ implies that the bottom water conditions in the Landsort Deep have not always been anoxic. We have added a statement to make that clear in the text (page 9905 line 14): "[. . .] deep pore water source of dissolved Mn2+. Such a deep source is expected to be important at sites where abundant Mn has accumulated during previous periods of more oxic conditions."

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

reviewer comment:

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

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and duration of inflow events since the late 1970s.

Answer:

See our reply to a similar comment above.

Minor comments

reviewer comment: 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.

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

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

Answer: We refer to our reply to reviewer #1

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

Answer: We added this reference.

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

Answer: This is a conclusion not a suggestion.

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

Answer: We have replaced "sediment" by "water column"

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

Answer: We have made the suggested change.

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

Answer: We have added the names of the Faro deep and northern Gotland Deep to

the cross section.(see figure below)

Additional change: we have added a reference to the paper by Carstensen et al. (2014) in the introduction given its relevance to this study (page 9892, line 3).

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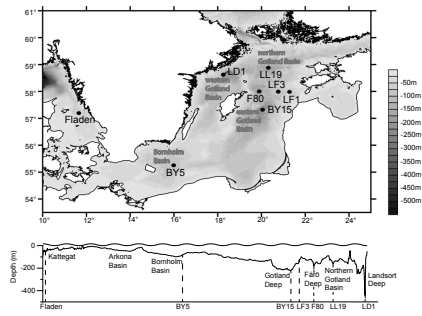
Fig. 1. Figure 1 Bathymetric map and depth profile of the Baltic Sea showing the locations of the sampling sites.

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