

Review of “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.

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:

-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.

-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.

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

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

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

-Page 8, line 28: Please find a more scientific term than “hand in hand”.

-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.

-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.

-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.

-Page 13, line 27: What does “their occurrence” refer to ? Reducing conditions ? Inflow ?

-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”.

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.

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 μM scale. The authors have done that for the solid-phase Mn data and it makes it much easier to read the plot.

Major comments:

-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.

-Page 8, line 20: Carman and Rahm (1997) use (asides from H_2S 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.

-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 \rightarrow high TOC and Mn solid accumulation rates \rightarrow 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.

-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.

-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.