Dear Dr. Leticia Cotrim da Cunha,

With this letter, we have uploaded the author´s response to the reviewer’s comments on the manuscript entitled:

“*Are recent changes in sediment manganese sequestration in the euxinic basins of the Baltic Sea linked to expansion of hypoxia?*” by “Lenz et al.”

Below is a detailed letter of reply to the reviewer´s comments divided into 3 parts. First the comments of the referees/public, second the point-by-point response and explanation of how and where each point raised by the reviewers was incorporated in the manuscript. Line numbers refer to the manuscript published in BGD. The third part consists of additional changes made (line numbers refer to the manuscript with the marked changes) and the revised manuscript with all changes marked.

Yours sincerely,
Conny Lenz

1. *Comments from referees/public*

Anonymous Referee #1

Received and published: 10 July 2014

The recent manuscript by Lenz et al. deals with a postulated impact of inceasing hypoxia in a temperate marginal sea, the Baltic Sea, on the formation conditions of Mn(II)-bearing carbonates. The latter have been considered to represent the very early diagenetic products after so-called inflow events, when oxygenated North Sea water is mixing with anoxic deep waters, thereby leading to the precipitation of the formally dissolved divalent manganese in form of Mn(IV)oxide layers. In principle this is a very interesting topic that is still not fully understood and of interest for the global scientific community.

The present authors carried out a detailed geochemical analyses of solid phases and pore waters from 210Pb-dated surface sediments from overall 7 Baltic Sea stations and another station that is positioned in the North Sea-Baltic Sea transitional area.

Although the topic is of high interest and the manuscript presents a large set of data, there are some major questions wrt. both the analyzed data as well as there interpretation:

In general 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). - In general 2: Most details facing analytical instruments, sensors, standards used, analytical precision etc. are missing in the Material & Methods part. -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 -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. -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 CO_2 produced compared to hydrogen sulfide. -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. -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 $MnCO_3$ and $CaCO_3$ were used for these calculations? Solid-solutions are the actual phases with solubility products deviating from ideal mixtures (see above). What is the actual mineralogy considered by Emerson et al.(1983) for MnS? 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? -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 CO_2 (and if present H_2S) 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. -9900-18: Are these really Fe(III)-phosphates or actually FeOOH with adsorbed phosphate? -9901-5: Why ’now’? Isn0t this the general case for the Baltic deeps? -9901-16: The increase of supersaturation in $MnCO_3$ after inflow events was not shown by Meischner & Huckriede (1996), only assumed. -9901-25: reference? -9902-25: How can more reducing conditions yirld 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 $MnCO_3$ instead of MnS precipitation. -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 $MnCO_3$ precipitation? The reacion rate of H_2S von MnO_2 is very high and an increase in alkalinity will also lead to an enhanced $MnCO_3$ precipitation rate. -9904-23: Here it would be appropriate to refer to Neubert et al. (2008, Geology) and Nägler et al. (2011, Chem Geol). -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 $H_2S(aq)$, that was measured together with bisulfide in the pore water. 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? 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 Mn^{2+} 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.

Anonymous Referee #2

Received and published: 21 July 2014

Lenz and colleagues present sediment and pore water geochemical data for a number of (intermittently) anoxic basins (so-called Deeps) in the Baltic Sea. The purpose of their study is to characterize modes of Mn carbonate and sulfide formation with special emphasis on recent changes related to expanding hypoxia in the Baltic Sea since 1980. Several working groups investigated the formation of authigenic Mn carbonates in the Baltic Deeps in the 1990s and early 2000s. As a result of these precursor studies (Suess 1979, GCA; Sternbeck & Sohlenius, 1996; Huckriede and Meischner, 1996, GCA; Boettcher & Huckriede, 1997, Marine Geology; Neumann et al., 1997, Continental Shelf Research; Neumann et al., 2002, GCA; Heiser et al., 2001, Marine Geology; all cited in the manuscript), the general mechanism of Mn oxide formation during in- flow of well-oxygenated water from the North Sea and subsequent transformation to Mn carbonate after the recurrence of anoxia is reasonably well established. One of the afore-mentioned articles (Heiser et al., 2001, Marine Geology, cited in the manuscript) noted a low Mn burial efficiency after a short-lived oxygenation event during the otherwise predominantly anoxic 1990s. This observation is the major connecting factor for the present study.

Lenz et al. use state of the art methods and present a nice data set which is unprecedented in spatial coverage and temporal resolution. It therefore provides an excellent basis for studying how sedimentary Mn cycling has evolved since the early 2000s. Most of the findings presented are consistent with previous conclusions. The authors also claim to revise certain aspects of the previously published model for the formation of authigenic Mn minerals in the Baltic Sea. Some of the arguments for this revision do not seem well developed, however, and therefore require additional discussion. Below is a list of comments that I ask the authors to address.

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 fluxof _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.

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.

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.

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.

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).

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.

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.

Minor comments:

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. Page 9894, Line 25: I doubt that pH measurements after 30 minutes of centrifuging yield meaningful results. Page 9900, Line 11: Could add 'Scholz et al., 2013, Chemical Geology'. Page 9901, Line 8: Replace 'conclude' with 'suggest'. Page 9905, Line 5: Delete ‘sediment’ before ‘euxinia’. By definition, euxinia refers to the water column. Table 1 and 2: Add the names of the basins to the stations. Fig. 1: Add the names of all basins to the cross section.

2. *Authors response*

Response to reviewer 1

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 have been 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) CO3 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 have also modified the corresponding text in the discussion where we write (page 9901 line 14): "When bottom waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are typically undersaturated with respect to Mn-Ca solid solutions down to a depth of ~5 to 8 cm (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 additional information where relevant:

We now write:
Section 2.2. (page 9894-12): "greiner tubes"
Section 2.2. (page 9894-20): "ICP-OES (Perkin Elmer Optima 3000),
Section 2.2. (page 9894-25): "the pH with a pH electrode and meter (Sentron).
Section 2.2 now ends with: "All colorimetric analyses were performed with a Shimadzu spectrophotometer. Replicate analyses indicated that the relative error for the pore-water analyses was generally <10 %."
Section 2.3 (page 9895- 6): "Based on laboratory reference materials and replicates, the relative error for organic C was generally less than 5%."
Section 2.3 (page 9895-10): "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."

-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 in Geology (2013) 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, 2013). 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. We accept that these factors make LD1 the least well-dated of all cores in this study.

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.

-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 postulate that this is due to the much quicker return of high sulfide concentrations in the bottom water and surface sediments after an inflow event. The Mn oxides are thus more quickly exposed to high sulfide concentrations and as a consequence, are lost before Mn carbonates can form.

We have now changed the text in the abstract to make this clearer: "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."

-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.

-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, 2013; Geology).

-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).

Indeed, we find the same results as Carman and Rahm (1997), see answer to comment 1 (above).

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.

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. We are using this knowledge in our calculations given that its presence has been suggested.

-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; see above.

We have now added a statement about the effect of degassing on pH values in the methods section (9894 line 25): "Note that degassing may impact ex-situ pH measurements and may lead to a rise in pH (Cai and Reimers, 1993; L&O)."

-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.

To avoid confusion, 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.

-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 modified the sentence in line 5 to make this clearer: “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”.

-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: “However, strong oversaturation is assumed to be reached following the inflow of oxygenated, saline North Sea water”.

-9901-25: reference?

Here the reviewer refers to the sentence: ”We postulate the 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”.

Given that this is a postulation, we had not added references. We have now added an additional sentence, to further support our statements: “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).

-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 MnS formation and observe a correlation with Br and Mo that suggests a possible mechanistic link with the input of organic material and more reducing conditions. 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."

-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 6), it is likely that Mn oxides no longer survive long enough to allow for efficient retention of the Mn^{2+} as Mn-carbonate.

We have modified the text to make the link with the sulfide concentrations more clear: "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…"

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

The paper by Neubert only deals with Mo fractionation in the water column and thus is not so relevant here. The paper by Nägler et al. 2011 does mention the process of Mo scavenging by Fe and Mn oxides but does not draw a conclusion about the importance of this process for the burial of Mo in the sediment.

-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.

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^+) is 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.

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 further 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. 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 and concentrate on the remaining 7 sites.

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Response to reviewer 2

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.

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.

Here, we are not referring to the benthic release fluxes, i.e. the sediment-water exchange of Mn^{2+} 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 Mn^{2+} 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 Mn^{2+} 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 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" 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)."

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 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)."

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 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 […]."

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.

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."

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 (2013; Geology). 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.

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.

We agree that a deep source of dissolved Mn^{2+} 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 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."

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

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 a similar comment above.

Minor comments:

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.

Page 9894, Line 25: I doubt that pH measurements after 30 minutes of centrifuging yield meaningful results.
We refer to our reply to reviewer #1

Page 9900, Line 11: Could add 'Scholz et al., 2013, Chemical Geology'.
We added this reference.

Page 9901, Line 8: Replace 'conclude' with 'suggest'.
This is a conclusion not a suggestion.

Page 9905, Line 5: Delete 'sediment' before 'euxinia'. By definition, euxinia refers to the water column.
We have replaced "sediment" by "water column"

Table 1 and 2: Add the names of basins to the stations.
We have made the suggested change.

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

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

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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3. *author's changes in manuscript*

Additional changes: (page and line numbers refer to revised version with mark ups)

Page 2 line 13: we deleted *often*
Page 4 line 11: we replaced *benthic release* with *diffusive flux from the sediments*
Page 6 line 17ff.: we added the method of the new age model for F80:
The age model for F80 was constructed using high resolution Mo and Mn data. In 2013, an extra sediment core from this station was taken and mini sub-cores as described in section 2.4 were embedded in Spurr´s epoxy resin and measured by LA-ICP-MS. 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).
Page 6 line 28: *was* was deleted
Page 6 line 29: *samples* was replaced with *sub-cores*
Page 7 line 3: we insert the word *of*
Page 8 line 6f: the reference to the data and appendix was added:
Whenever possible (LF3, LL19, BY15 and F80) higher resolution data from the 2009 Aranda cruise was used for the calculation (table 2 and data in Appendix B).
Page 9 line10: the results of the saturation calculation was changed according to the new results:
Saturation indices for MnCaCO3 are positive below the surface sediment at the Landsort Deep, indicating supersaturation of the pore water with respect to this mineral. The other hypoxic and anoxic sites except LF3 reach saturation only at greater depth.
Page 9 line 17: we added: *and in the anoxic Landsort Deep (LD1)*
Page 10 lines 14-17: to improve the link between text and figure we added the color code of the figure in the text: *in the RGB composite … Mn (red) and S (blue) … Ca (green)*
Page 10 line 24: As a result of the discussion with the reviewer 1, we deleted: *Our calculated diffusive fluxes suggest that some dissolved Mn likely still escapes to the overlying water (Table 2).*
Page 11 line 8: *benthic* was replaced with *diffusive*
Page 11 line 24: we added *the*
Page 12 line 4: we added *bearing*; and *B*asin and *D*eep were written with capital letters
Page 12 line 7: we changed *Mn carbonate* to *Mn(Ca) carbonates*
Page 12 line 28: *a* was changed to *ä* in Matthäus
Page 12 line 29: we deleted: *Our results confirm that*
Page 12 line 31: the sentence was rephrased to: *In the Landsort Deep, Lepland and Stevens (1998) attributed the enrichments to the relatively high alkalinity.*
Page 13 line 17: *our* was replaced by *the*
Page 14 lines 5-6: we changed the figure 6, therefore the text was changed from *F80* to *LL19*
Page 17 lines 5-6 we added: *We thank Simon Veldhuijzen for his contribution to the analyses for site F80.*
Page 32 Figure 6 we replaced the plots of F80 with LL19
We added the age model of F80 in appendix A. Furthermore, an appendix B with the pore water and sediment data used for the figures 2 and 4 was created.

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

C. Lenz[1,2], T. Jilbert[2], D.J. Conley[1], M. Wolthers[3,2] and C.P. Slomp[2]

[1]{ Department of Geology, Lund University, Sölvegatan 12, SE-22362 Lund, Sweden}

[2]{Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, the Netherlands}

[3]{University College London, Department of Chemistry, 20 Gordon Street, London, WC1H 0AJ, United Kingdom}

Correspondence to: C. Lenz (conny.lenz@geol.lu.se)

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 consequences of the expanding hypoxia for manganese (Mn) burial in the Baltic Sea using a combination of pore water and sediment analyses of well-dated sediment cores from 8 locations. Diffusive fluxes of dissolved Mn from sediments to overlying waters at oxic and hypoxic sites are in line with an active release of Mn from these areas. However, this flux of Mn is only 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 form independent of inflow events, with pore water Mn produced in deeper layers of the sediment acting as a key Mn source. While formation of Mn enrichments in the Landsort Deep continues to the present, this does not hold for the Gotland Deep area. Here, increased euxinia, as evident from measured bottom water sulfide concentrations and elevated sediment molybdenum (Mo), goes hand in hand with a decline in sediment Mn and recent

inflows of oxygenated water (since ca. 1995) are no longer consistently recorded as Mn carbonate layers. 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. ~~We postulate that the reduction of Mn oxides by hydrogen sulfide following inflows has become so rapid that Mn^{2+} is released to the water column before Mn carbonates can form.~~ Our results have important implications for the use of Mn carbonate enrichments as a redox proxy in marine systems.

1 Introduction

Manganese (Mn) enrichments in sedimentary deposits are often 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 ~~often~~ associated with calcium and can contain other impurities (e.g. Jakobsen and Postma, 1989; Manheim, 1961; Sternbeck and Sohlenius, 1997; Suess, 1979). These minerals are suggested to form from Mn oxides deposited during a period 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 both mineral phases is assumed to be driven by an exceptionally high alkalinity, with Mn sulfides forming when H_2S exceeds Fe availability (Böttcher and Huckriede, 1997; Lepland and Stevens, 1998). Finally, Mn enrichments may also 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; Mercone et al., 2001). 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).

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, that are especially 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, 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.

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, 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 an authigenic mineral, is termed the "Mn shuttle" (Lyons and Severmann, 2006).

In a basin with expanding hypoxia and anoxia, as is the case in the Baltic Sea over the past century (Conley et al., 2009), the Mn shuttle is expected to have become more efficient in transporting Mn to deeper, euxinic basins because of decreased trapping of Mn in oxygenated surface sediments (Lyons and Severmann, 2006). We postulate that, during the first phase of the expansion of bottom water hypoxia, there may even have been a "pulse" of release of Mn from the sediments. During an extended period of hypoxia and anoxia, however, sediments in hypoxic areas may become depleted of Mn oxides, thus reducing the strength of the Mn shuttle. In addition, the formation rate of authigenic Mn minerals at deep basin sites may change in response to hypoxia and anoxia. If dissolved Mn^{2+} is the dominant control for Mn carbonate formation as suggested for the Gotland Deep (Neumann et al., 2002), expanding anoxia could 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 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 could be similar or increase due to higher rates of sulfate reduction.

In this study, we use geochemical analyses of well-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 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 ~~benthic release~~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 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 in many deep basin sites suggests that inflows of oxygenated seawater are no longer recorded by Mn carbonate deposits.

2 Materials and Methods

2.1 Study area

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, F80 and LD1, are situated below the redoxcline, which was located between 80 and 120 m water depth at the time of sampling. Therefore, these sites are all currently 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 (Baltic Sea Environmental Database at Stockholm University; http://nest.su.se/bed/ACKNOWLE.shtml).

2.2 Bottom water and pore water analyses

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 and S were acidified with either HNO_3 (Fladen, BY5) or HCl (all other stations) and stored at 5°C until further analysis with ICP-OES (Perkin Elmer Optima 3000; relative precision (<5%) and accuracy were established by standards (ISE-921) and duplicates). Hydrogen sulfide was assumed to be released during the initial acidification, thus S is assumed to represent SO_4^{2-} only. Total Mn is assumed to represent Mn^{2+}, although 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 may impact ex-situ pH measurements and may lead to a rise in pH (Cai and Reimers, 1993). The total alkalinity ~~and~~ was then titrated ~~for total alkalinity~~ 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 %.

2.3 Sediment analyses

Sediment samples were freeze-dried and water contents were calculated from the weight loss. 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 mg of sediment was decalcified with 1M HCl and the C content was determined with a Fisons NA 1500NCS. Based on laboratory reference materials and replicates, the relative error for organic C was generally less than 5%. Total sediment contents of S, Mn and Mo were determined with ICP-OES, after dissolution of 0.125 mg 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. 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.

Age models based on ^{210}Pb analyses for 6 multi-cores used in this study have been previously published. For details, we refer to the relevant papers: Fladen and BY5 (Mort et al., 2010), LF1 and LF3 (Jilbert et al., 2011)~~, and~~ LL19 ~~and F80~~ (Zillén et al., 2012) and BY15 (Jilbert and Slomp, 2013). A n~~N~~ew ^{210}Pb age model~~s~~ ~~were~~ was constructed for ~~BY15 and~~ LD1. ~~Samples from BY15 were analyzed by α-spectrometry as described in Jilbert et al. (2011).~~ Samples from 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 BY15 and~~for LD1, we refer to the supplementary information Appendix A. The age model for F80 was constructed using high resolution Mo and Mn data. In 2013, an extra sediment core from this station was taken and mini sub-cores as described in section 2.4 were embedded in Spurr´s epoxy resin and measured by LA-ICP-MS. 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).

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 by Jilbert and Slomp (2013). 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 ~~was~~ compacted resulting in a reduction of length of both sections by up to 50%. After curing, epoxy-embedded ~~samples~~ 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 extended to the original length of the core section and aligned to the samples data for the same depth interval (not shown).

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 ~~(not included in Figure 2)~~ with Fick's first law:

$$J_{sed} = -\varphi * D_{sed} * (\delta C/\delta x)$$

where φ is the porosity, D_{sed} is the whole sediment diffusion coefficient, C is the Mn concentration and x is depth in the sediment. D_{sed} was calculated from the diffusion coefficient in free solution corrected for salinity and temperature (D^{SW}) and porosity (Boudreau, 1997):

$$D_{sed} = D^{SW} / 1 - \ln(\varphi^2)$$

Whenever possible (LF3, 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

~~Saturation indices for rhodochrosite (Mn carbonate), calcite (Ca carbonate) and Mn sulfide were calculated~~ Thermodynamic equilibrium calculations have been performed for the pore water ~~for~~ of LF3, LL19, BY15, F80 and LD1 ~~sites~~ using version 3.1.1 of the computer program PHREEQC (Parkhurst and Appelo, 1999) with the LLNL database. The database 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 carbonates. 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. ~~and t~~The solubility of iron sulfide from Rickard (2006) ~~and an equilibrium constant pK of 0.377 for Mn sulfide from Emerson et al. (1983).~~ was added to the calculations as well as $MnHS^+$ ~~was also added~~ 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).

3 Results

At the time of sampling, bottom waters were oxic at the Fladen and LF1 sites, 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). At the Fladen site, however, Mn^{2+} concentrations decrease again below ca. 5 cm and at sites LF1 and LF3, Mn^{2+} is nearly absent. Alkalinity and ammonium concentrations increase with sediment depth, with the increase going hand in hand with a decline in sulfate. 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. Saturation indices for ~~rhodochrosite and calcite~~$MnCaCO_3$ are ~~> 0~~positive below the surface sediment at the Landsort Deep~~all hypoxic and anoxic sites except LF3~~, indicating supersaturation of the pore water with respect to ~~these~~ this mineral~~s in the various basins~~. The other hypoxic and anoxic sites except LF3 reach saturation only at greater depth. For Mn sulfide, in contrast, supersaturation is only observed at the Landsort Deep site, LD1 (Figure 3) and below 35 cm at site F80. Calculated diffusive fluxes of Mn^{2+} vary over a wide range, 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 when compared to LF1 and BY5 (Table 1; Figure 4). Sediments are 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. 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, 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 but is enriched at the other sites, where profiles largely follow those of TOC.

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

In the surface sediments of station 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 RGD 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).

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 (Fig. 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. ~~Our calculated diffusive fluxes suggest that some dissolved Mn likely still escapes to the overlying water (Table 2).~~ 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 the sites on the slope of the eastern Gotland Basin (LF1 and LF3), in contrast, the sediments are nearly completely devoid of Mn, both in the pore water and solid phase. This highlights that while sediments in some hypoxic areas, such as the Bornholm Basin, may still 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, 2013; Lyons and Severmann, 2006; Scholz et al., 2013), sediments in some shallow areas no longer do so.

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 dissolution of Mn oxides or Mn carbonates (e.g. Heiser et al., 2001; Jilbert and Slomp, 2013). As a result, ~~benthic~~ diffusive Mn fluxes 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 ~~Fe-(III)-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 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~~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.

4.2 Manganese sequestration in the anoxic basins

Formation of Mn bearing carbonates in the Gotland ~~basin~~ Basin and Landsort ~~deep~~ Deep is generally described as being ubiquitous (e.g. Jakobsen and Postma, 1989). When bottom waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are typically undersaturated with respect to Mn(Ca) carbonates down to a depth of ~5 to 8 cm (Figure 3)(Carman and Rahm, 1997; Heiser et al., 2001). However, strong oversaturation ~~may~~ is assumed to be reached following the inflow of oxygenated, saline North Sea water (Huckriede and Meischner, 1996; Sternbeck and Sohlenius, 1997). 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 (Fig. 4). ~~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 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 the sediment-water interface. Furthermore, these Mn carbonate enrichments occur independently of enrichments in Mo and S, suggesting relatively oxic conditions at the time of precipitation. Both lines of evidence support the interpretation of Mn carbonate precipitation within a very short time, possibly only weeks, 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 (Fig. 5) correspond to inflows in 1993 and 1997 (Matth~~a~~äus and Schinke, 1999).

~~Our results confirm that~~ 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) ~~This was~~

attributed the enrichments to the relatively high alkalinity ~~at this site (Lepland and Stevens, 1998)~~. Our pore water results show that the alkalinity is similar to that of F80. However, the pore water Mn^{2+} concentrations 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. 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.

~~Our~~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 ~~at this site~~ (Fig. 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 (Fig. 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 (Fig. 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 the MnS formation ~~implying rapid changes in Mn mineralogy in response to seasonal variability of the organic matter flux (Fig. 5)~~. 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.

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 (Baltic Sea Environmental Database in Gustafsson and Medina (2011)) for sites in the northern Gotland Basin (LL19)~~F80~~ and the Landsort Deep (LD1) (Figure 6). At site ~~F80~~LL19, Mn enrichments in the sediments coincide with low values of Mo in the sediment and inflows of oxygenated water. At LD1, in contrast, high Mn contents are observed from 1965 onwards, independent of inflows, with the highest Mn values coinciding with the most euxinic periods, which mostly occurred after the year 2000.

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 6), are accompanied by a strong reduction in sediment Mn burial. 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). ~~For example,~~However, at ~~F80~~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 6)~~. Similarly, at LL19, the inflow in 2003 is not recorded by a Mn carbonate layer in the high resolution geochemical analyses~~, 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. ~~are clearly visible in both the LA-ICP-MS and micro-XRF scans (Figure 5).~~ 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.

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). 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). 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. ~~reducing conditions in the bottom waters and surface sediments linked to the expansion of hypoxia and euxinia.~~ 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. ~~Given that, i~~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).~~, these results further imply~~ 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~~are likely not the main carrier of Mo to the sediment in the Baltic Sea as suggested recently for the Gotland Deep (Scholz et al., 2013)~~.

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 ~~sediment~~ 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, 2013) 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 indicate that Mn enrichments may also form frequently in an anoxic basin as Mn carbonates and sulfides 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. Mn enrichments in geological deposits thus can be indicative of both oxic and anoxic depositional environments, emphasizing the need for multiple redox proxies.

5 Conclusions

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. 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 Mn^{2+} is lost to the water column. In Landsort Deep, in contrast, Mn sulfides and carbonates are still being precipitated. This is attributed to an additional diffusional source of Mn from deeper pore water. Our results indicate that sediment Mn carbonates in the Baltic Sea no longer reliably record inflows of oxygenated North Sea water. This has implications for the use of Mn enrichments as a redox proxy when analyzing geological deposits.

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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. Negative O_2 values indicate the presence of H_2S assuming that 1 mol of H_2S is equivalent to 2 mol O_2. 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 Sept. 2007	57°11.57N 11°39.25E	82	1.0	oxic	34.2
LF1	Northern Gotland Basin	R/V Aranda May/June 2009	57°58.95N 21°16.84E	67	0.25	oxic	8.2
BY5	Bornholm Basin	R/V Skagerak Sept. 2007	55°15.16N 15°59.16E	89	0.23	O_2=0.09 mLL^{-1}	16.2
LF3	Eastern Gotland Basin	Sediment: R/V Aranda May/June 2009 Pore water: R/V Pelagia May 2011	57°59.50N 20°46.00E	95	0.50	O_2=-0.13 mLL^{-1}	10.1
LL19	Northern Gotland Basin	Sediment: R/V Aranda May/June 2009 Pore water: R/V Heincke July 2010	58°52.84N 20°18.65E	169	0.30	O_2=-0.89 mLL^{-1}	11.4
BY15	Gotland Deep	Sediment R/V Aranda May/June 2009 Pore water: R/V Heincke July 2010	57°19.20N 20°03.00E	238	0.27	O_2=-3.32 mLL^{-1}	12.5
F80	Fårö Deep	Sediment: R/V Aranda May/June 2009	58°00.00N 19°53.81E	191	0.~~50~~55	O_2=-2.04 mLL^{-1}	12.0

		Pore water: R/V Heincke July 2010					
LD1	Landsort Deep	R/V Pelagia May 2011	58°37.47N 18°15.23E	416	0.77	anoxic and sulfidic	10.6

Table 2. Diffusive fluxes of Mn across the sediment-water interface at all 8 sites. For further details, see text.

Site	**Location**	**Year and cruise**	**Depth range cm**	**Diffusive Mn flux µmol m^{-2} d^{-1}**
~~Fladen~~	~~71~~			
LF1	Northern Gotland Basin	2009 R/V Aranda	BW-0.25	115
BY5	Bornholm Basin	2009 R/V Aranda	BW-0.5	236
LF3	Eastern Gotland Basin	2009 R/V Aranda	BW-1	0
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	~~131~~~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.

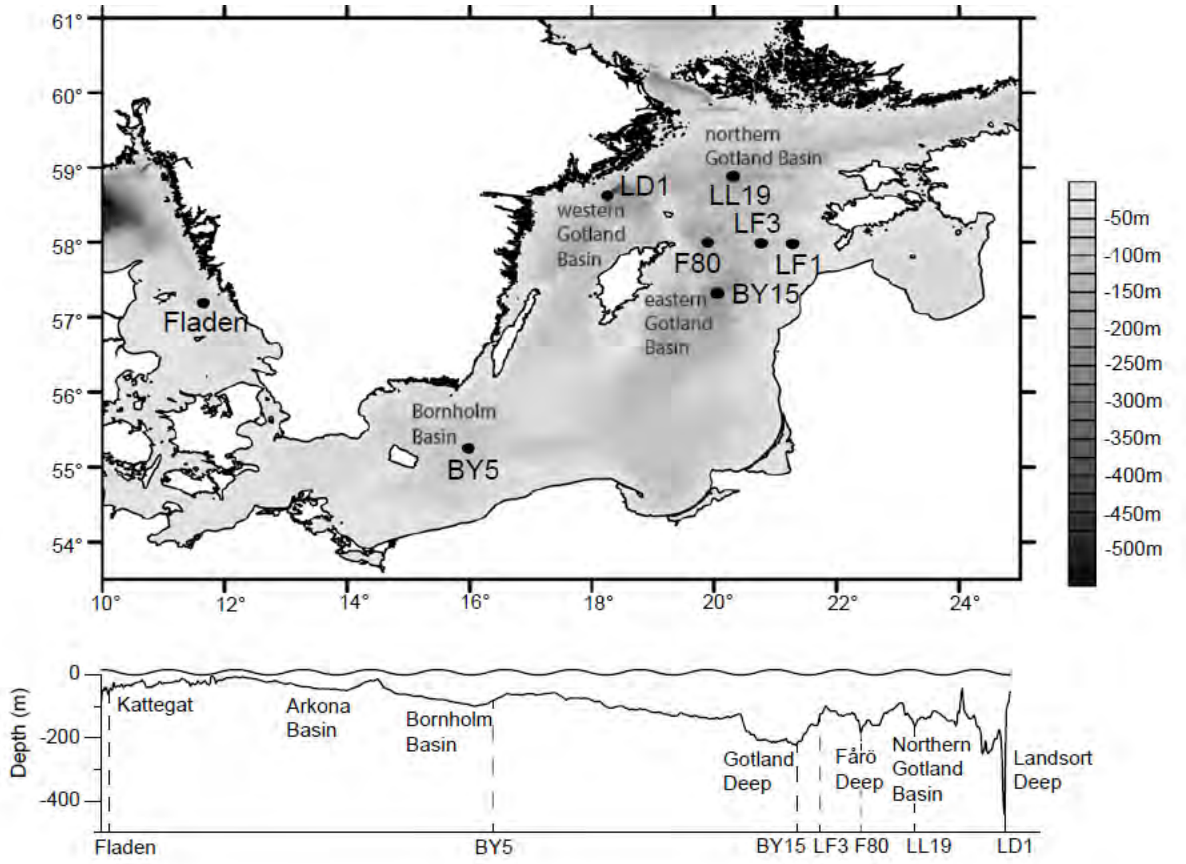

Figure 1 Bathymetric map and depth profile of the Baltic Sea showing the locations of the sampling sites.

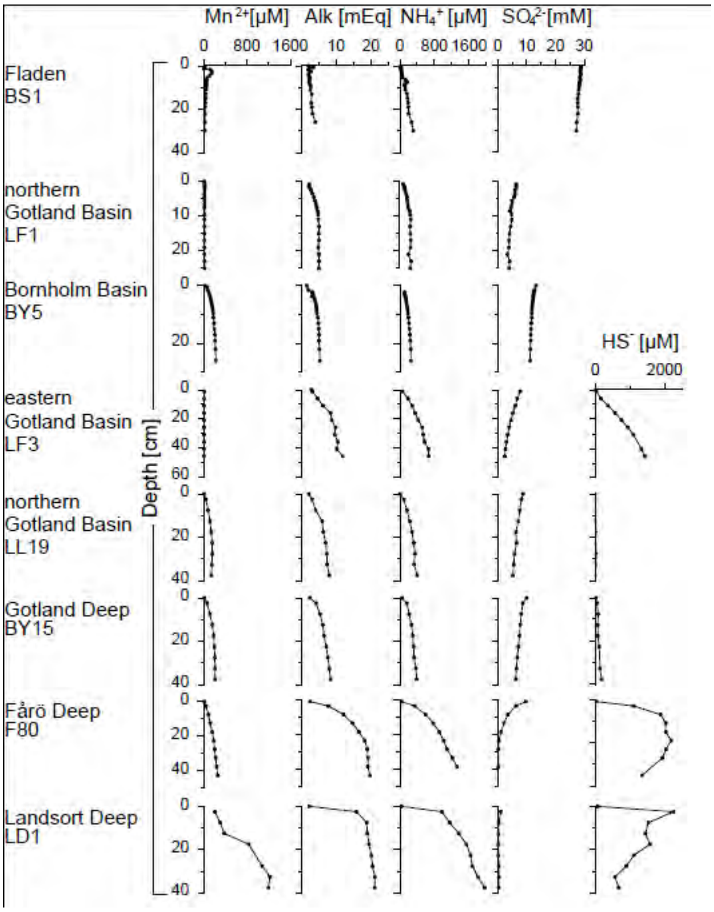

Figure 2 Pore water profiles of manganese (II), alkalinity, ammonium and sulfate for all 8 sites and hydrogen sulfide for the 5 deepest sites. Note, while dissolved sulfide is here expressed as HS$^-$, some H_2S is present as well.

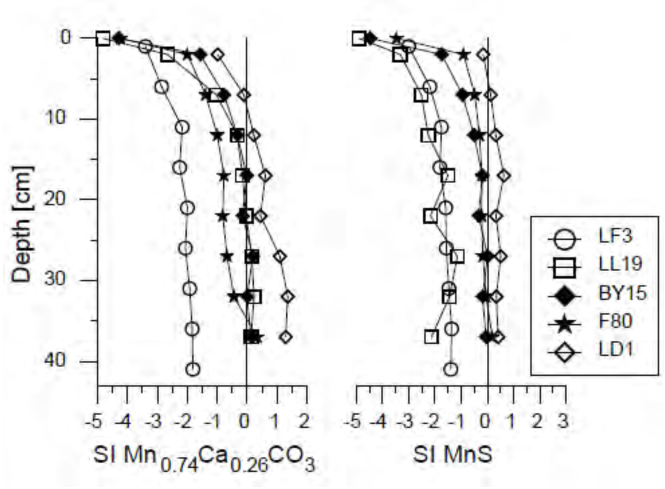

Figure 3 Saturation indices (SI) for $Mn_{0.74}Ca_{0.26}CO_3$ and MnS~~, rhodochrosite ($MnCO_3$), and calcite ($CaCO_3$)~~ as calculated from the pore water data with PHREEQC.

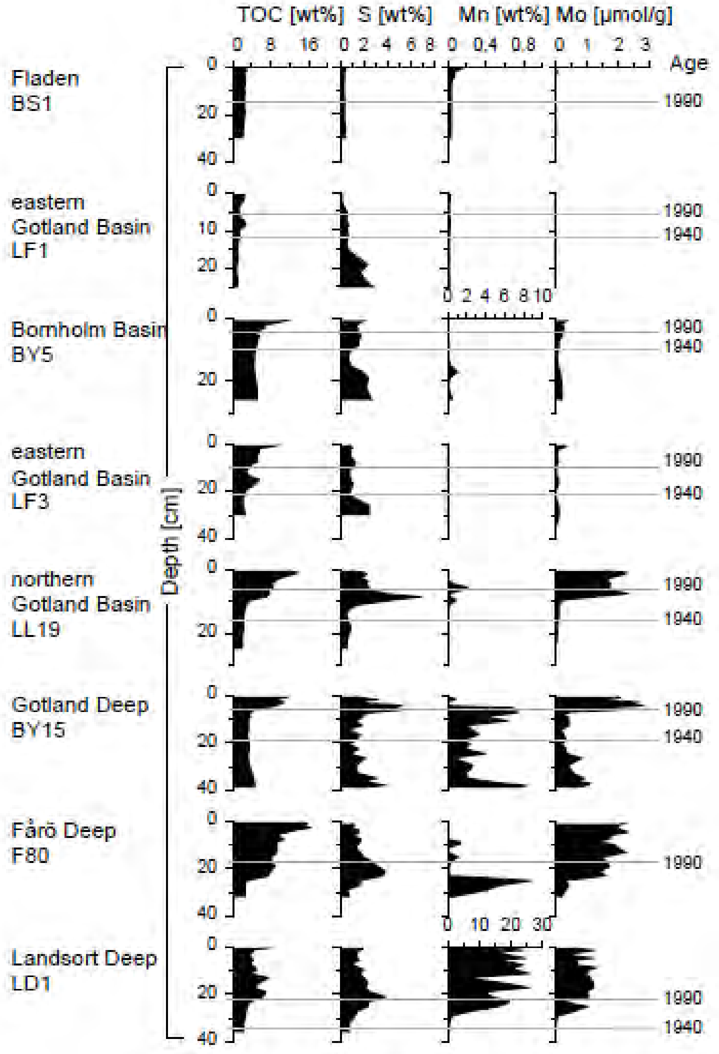

Figure 4 Sediment depth profiles of total organic carbon (TOC), sulfur (S), manganese (Mn) and molybdenum for all 8 sites. Note the different scale for manganese at Fladen and LF1, and LD1. Grey lines indicate the years 1990 and 1940, based on sediment dating. These date markers are used to demonstrate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

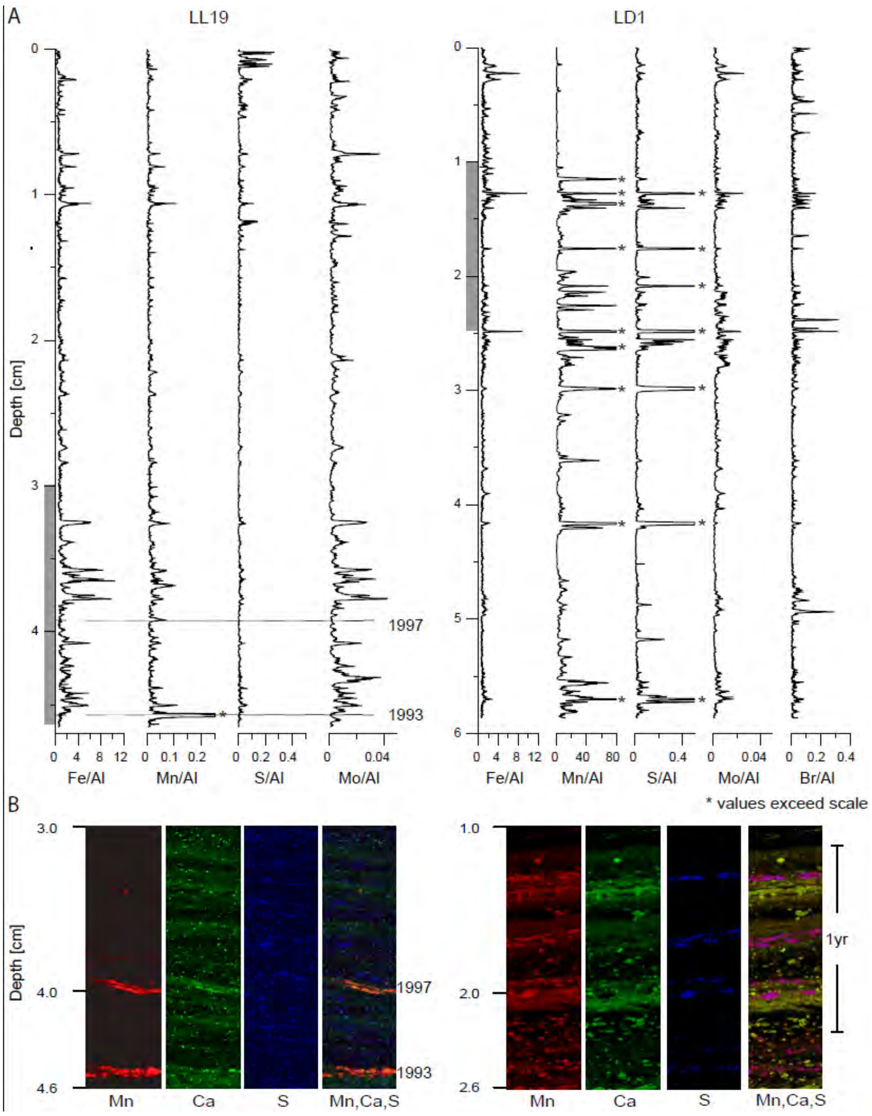

Figure 5 A: High resolution elemental profiles of Fe/Al, Mn/Al, S/Al, Mo/Al and Br/Al (only LD1) generated by LA-ICP-MS line scanning for resin-embedded surface sediment blocks. Note the difference in absolute values for Mn/Al between LL19 and LD1. The depth scale refers to the compacted sediment in 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.

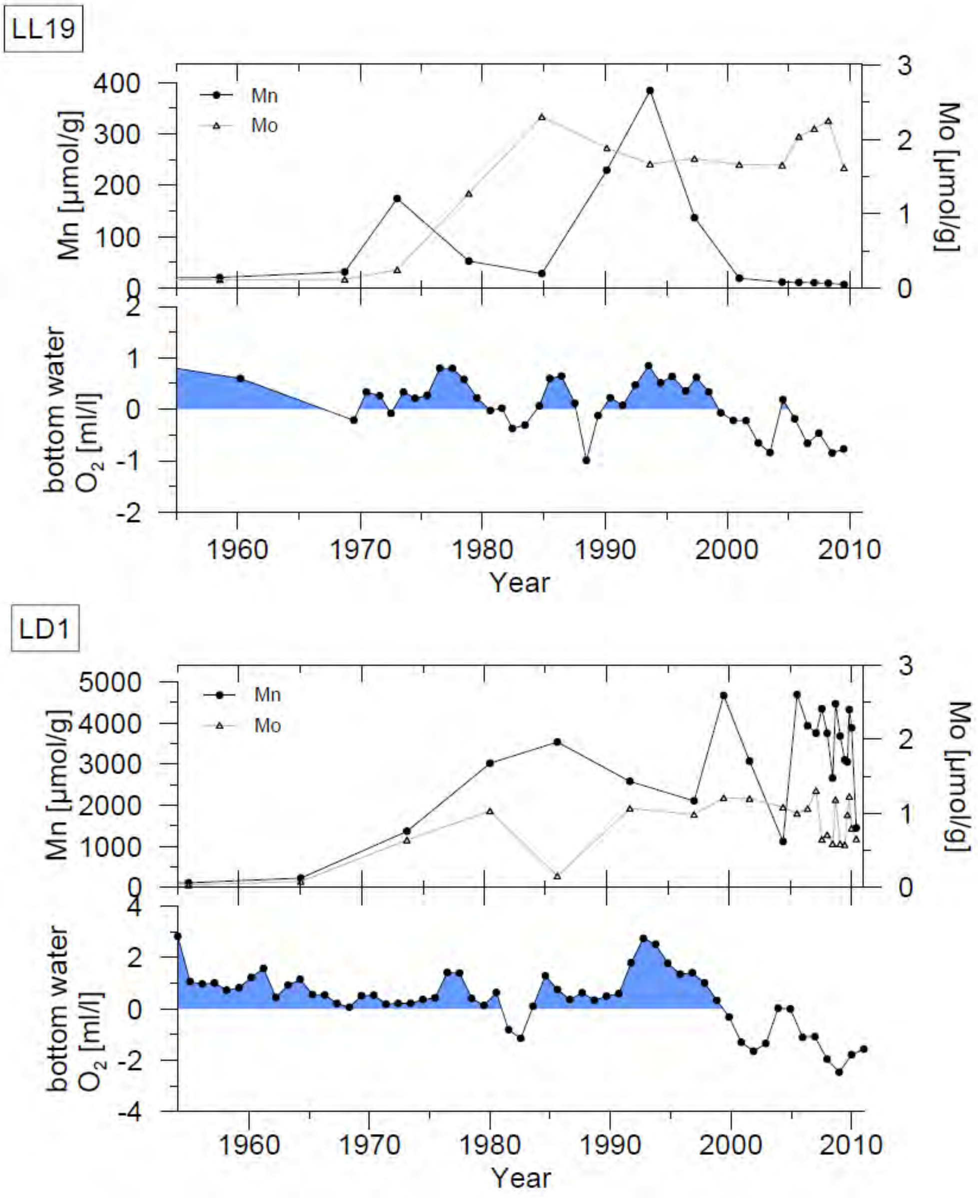

Figure 6 Records of sediment manganese and molybdenum for 1955-2010 for core ~~F80~~ LL19 and core LD1 and corresponding bottom water oxygen (Baltic Sea Environmental Database at Stockholm University; http://nest.su.se/bed/ACKNOWLE.shtml). Negative O_2 values indicate the presence of H_2S assuming that 1 mol H_2S is equivalent to 2 mol O_2.