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A mid-Holocene geochemical record of saline inflow to the Gotland Deep, Baltic Sea

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Abstract: The formation of Mn-enrichments in Gotland Deep sediments has been linked to the occurrence of periodic inflows of saline water from the North Sea. In turn these saline inflow events are very strongly linked to variation in North Atlantic atmospheric conditions. Here sedimentary Mn-concentrations in mid-Holocene sediments are measured with a 0.5 mm sampling resolution using scanning electron microscope techniques. As the sedimentation rate in core 20001-5 was estimated to be approximately 0.5–1 mm per year, examining the variation in Mn-enrichments may potentially provide an annual record of variation in saline inflow, and by extension, North Atlantic climate on interannual timescales. There are many processes that can affect Mn-cycling in the Gotland Deep. When considered together, these processes could potentially act to remove or significantly weaken the transmission of the primary saline inflow signal to the measured geochemical record, producing an effectively random Mn-record. Analysis of the Mn-record as a time series of discrete events revealed that the Mn-record was not consistent with a random distribution of events, and contains some long-term order. Spectral analysis of the Mn-record then indicates a significant periodicity in the Mn-record between 33 and 35.5 mm. This represents a discrete decadal periodicity in Mn-enrichment at 25–55 years that is consistent with the timing of previously reported Mn-enrichments in Gotland Deep sediments.

Key words: Saline inflows, Mn-carbonate, laminated sediments, time-series analysis, Mid-Holocene, Gotland Deep, Baltic Sea.

Introduction

Major inflows to the Baltic Sea have occurred regularly throughout the twentieth century (Matthäus, 1995) and have been related in many studies to the presence of Mn-enrichment in Gotland Deep sediments in the form of diagenetic Ca-rhodochrosite laminae (Burke and Kemp, 2002; Huckriede and Meischner, 1996; Neumann *et al*., 1997; 2002; Sohlenius *et al*., 1996; Sternbeck and Sohlenius, 1997). These saline inflow events are the product of North Atlantic atmospheric processes that culminate in overflows of saline water to the Baltic Sea at the Darss Sill. Saline inflows occur solely in winter, when westward wind systems, associated with blocking high-pressure areas, force water out of the Baltic Sea into the Danish straits causing a drop in Baltic Sea level (Matthäus and Schinke, 1994). This set-up period is then followed by the main inflow period itself, when a switch to eastward winds, associated with cyclonic activity, causes saline Belt Sea water to flow back into the Baltic Sea (Matthäus and Schinke, 1994). Schinke and Matthäus (1998) report that saline inflow occurrence is significantly greater in years with low surface runoff, which causes higher salinity in the Belt Sea; and in years with overall lower cyclonic activity, which causes set-up periods to occur more frequently.

Variation in the North Atlantic Oscillation (NAO) is reported to control much of the interannual climatic variability observed in the North Atlantic region (Marshall *et al*., 2001). The NAO was first described as variation in the zonal circulation (low-pressure difference between Azores High and Icelandic Low) by Walker and Bliss (1932), and is now commonly defined as the difference in the mean winter sea-level pressure between the Azores High and the Icelandic Low (Hurrell, 1995). Conditions favourable for saline inflow are associated with negative NAO index winters when lower cyclonic activity, reduced precipitation and more blocking highs occur in the Baltic region (Nesterov, 1998; Rogers, 1997). Börngen *et al*. (1990) reported that there is some coherence between records of saline inflow occurrence and the North Atlantic meridional circulation. The NAO has also been

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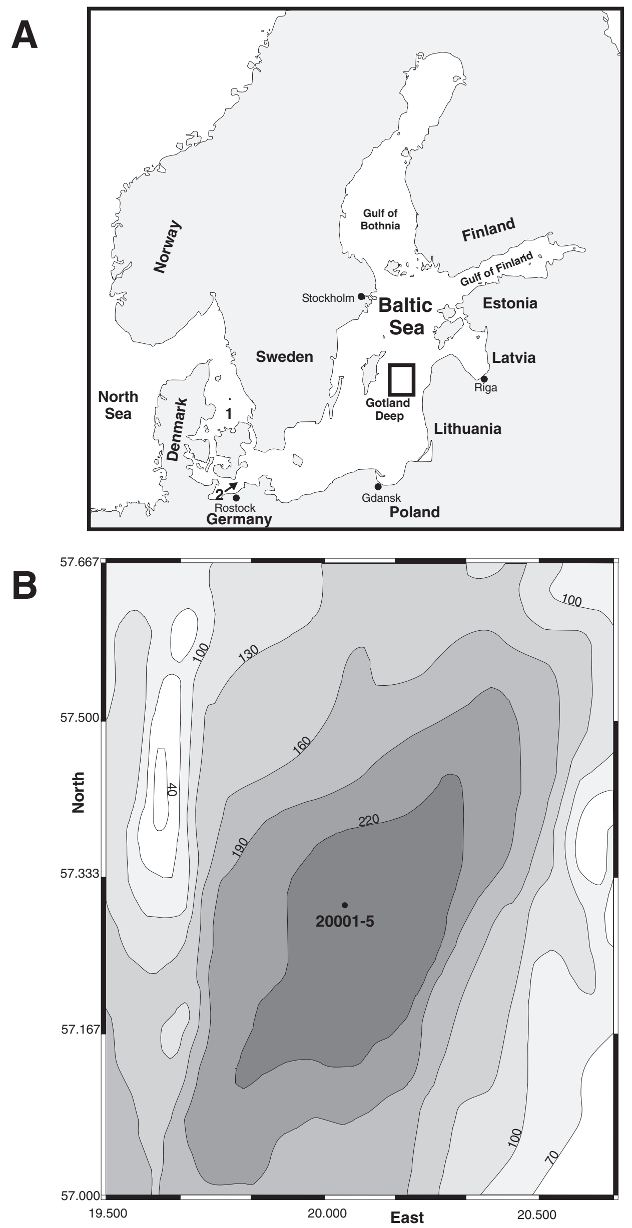

Figure 1 (A) Map of the Baltic Sea showing location of (1) Belt Sea and (2) Darss Sill. (B) Bathymetry of the Gotland Basin (after Emeis and Struck, 1998), and core location for 20001-5.

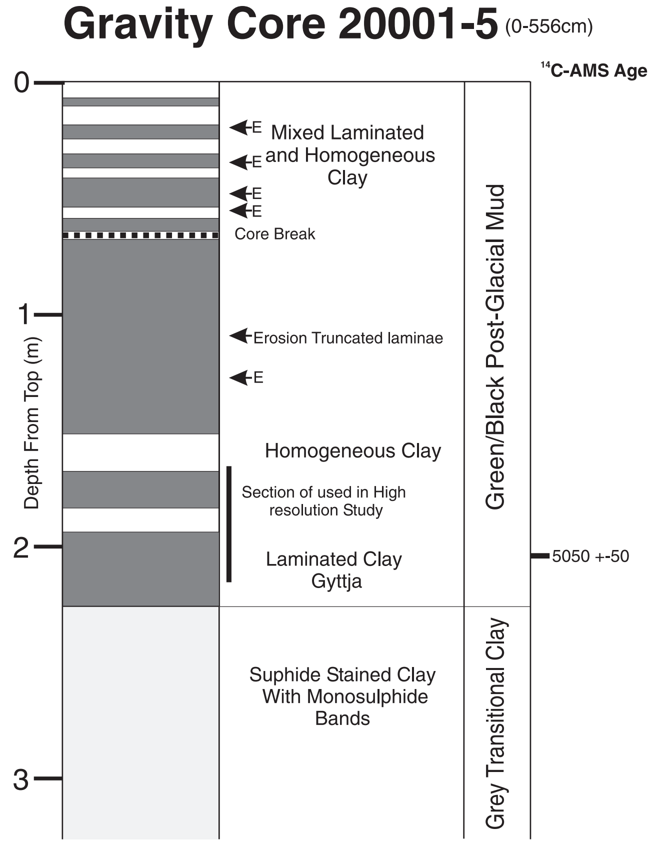

Figure 2 Lithology and stratigraphy of Gotland Deep core 20001-5, logged from X-ray images in Emeis and Struck (1998) by I.T. Burke., showing the section of core chosen for detailed study. Dark grey indicates laminated clay gyttja, light grey indicates sulphide stained clay and white indicates homogenous clay.

implicated in observed variations in the frequency of bottom-water renewal in Swedish fjords (Nordberg *et al*., 2000) and the Baltic Sea itself (Hänninen and Vuorinen, 2000).

Sedimentary Mn-enrichments were used as a proxy for saline inflows occurring in the past 250 years by Neumann *et al*. (1997); however, no studies as yet have investigated this relationship in mid-Holocene sediments beyond the extent of historical records. The scanning electron microscope (SEM) methods developed at Southampton have enabled the identification and use of recurring thin laminae (down to *c*. 20 microns) within varves for palaeoreconstruction. Hitherto, such lamina components have typically been diatomaceous or terrigenous (e.g., Bull and Kemp, 1995; Dean *et al*., 2001; Pike and Kemp, 1997). Here for the first time we use evidence from a lamina formed by chemical precipitation to aid in palaeoenvironmental reconstruction. Energy Dispersive X-ray Microanalysis techniques, used under the SEM, produce records in which the Mn-enrichment due to individual Ca-rhodochrosite laminae can be delimited, representing higher resolution than previous studies. This study, therefore, aims to assess the processes that affect Mn-enrichment in mid-Holocene Gotland Deep sediments and to determine the suitability of Mn-enrichments as proxy records of interannual- and decadal-scale variance in saline inflow events.

Methods and materials

As part of the Gotland Basin Experiment (Emeis and Struck, 1998), a 5.64 m gravity core, 20001-5, was collected in the Central Gotland Basin at 57°18.33'N, 20°03.00'E (Figure 1), in a water depth of 243 m, during cruise 94.44.13.2 of R/V *Alexander Von Humboldt* in August 1994. Initial core description and subsampling was undertaken by staff of the Institute of Baltic Research at Warnemünde, Germany, where the core was subsampled into 25 cm wet sediment slabs and X-ray exposures were taken. The wet sediment slabs were vacuum-packed in polythene bags to prevent desiccation. A radiocarbon ^{14}C-AMS age was obtained from a fish bone recovered from 205 cm in core 20001-5 for Dr U. Struck (Institute of Baltic Research, Warnemünde), with a reservoir correction of −400 yrs. Preliminary fabric descriptions were prepared from X-ray images in Emeis and Struck (1998) for the post-Ancylus sections of core 20001-5 (Figure 2).

Sediment samples from 165–216 cm were prepared for SEM study by embedding in epoxy resin using a fluid displacive impregnation technique modified from that described in Pike and Kemp (1996) by Kemp *et al*. (1998). Fluid displacive embedding allows thin-section preparation with minimal fabric

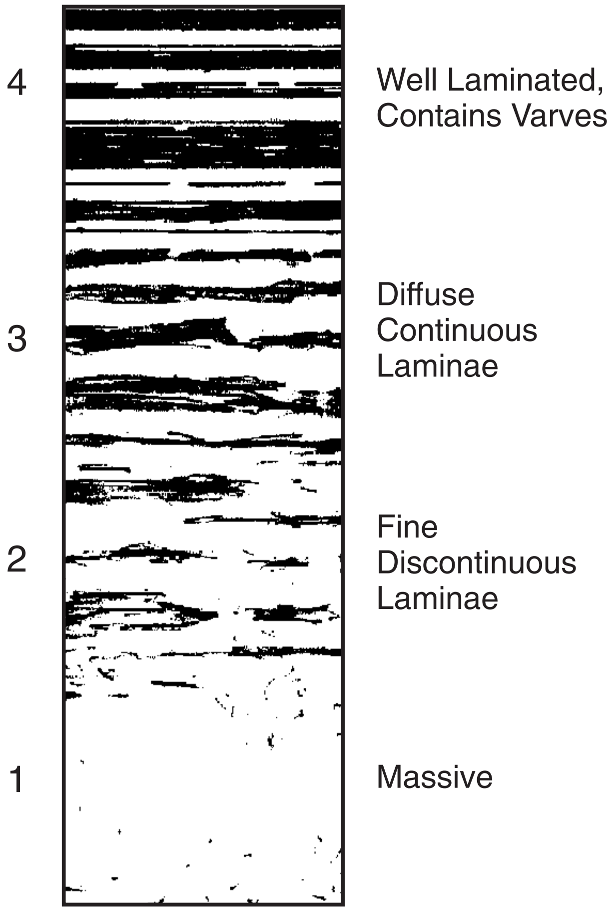

Figure 3 Bioturbation index based on sediment fabric disturbance (after Behl and Kennett, 1996).

disturbance. Polished thin sections were prepared using an oil-based lubricant. The polished thin sections were examined in the SEM using nondestructive back-scattered electron (BSE) imagery, and nondestructive major element analysis was performed on thin sections using the Energy Dispersive X-ray Microanalysis (EDS) tool fitted to the SEM under standard conditions (count time 40 sec; voltage 15 kV; beam current 5×10^{-6}A). Comparison to standard spectra produced quantitative data with errors of less than 10% down to 0.5 wt%; below 0.5 wt% errors can increase up to 25%. The sampled excitation volume using this technique can be as little as 2 μm^3. A 2 μm^3 spot analysis can be used to determine individual grain composition, but a 500 μm^2 raster was used in this study to average compositional data over a greater area and produce a better representation of the composition of individual laminae, or bundles of laminae. Profiles were produced by analysing a row of contiguous 500 μm^2 rasters.

A bioturbation index (Figure 3) was established for Gotland Deep sediments following the scheme of Behl and Kennett (1996), where sediment fabric is linked to the tolerance of burrowing organisms to variations in benthic oxygenation levels. The bioturbation index values were produced by visual inspection of low magnification ($\times 5$) back-scattered electron images. A bioturbation index of 4 equates to very well-laminated sediment fabric and benthic oxygen levels < 0.1 ml per litre. Conversely, at index level 1, the sediments are completely homogenized by benthic organisms, indicating oxygen levels > 0.3 ml per litre. This index is relatively sensitive to changes between oxic and anoxic benthic conditions, but does not record extremes in either oxic or anoxic conditions.

Mean sedimentation rate in core 20001-5

The upper part of core 20001-5 contains much evidence for erosion, in the form of truncated laminae on both macro (Figure 2) and micro (SEM) scales (Burke *et al*., 2002), and the position of core 20001-5 in the Gotland Deep is prone to erosion (Sivkov *et al*., 1998). Thus, it is likely that the apparent bulk sedimentation rate for this core of approximately 0.28 mm/yr (Christiansen and Kunzendorf, 1998) is not representative of the actual pre-erosion sedimentation rate. These erosional features were not observed in lower parts of core 20001-5, and this lower interval may, therefore, represent a coherent and continuous record of sedimentation. On this basis, a 51 cm interval from 165–216 cm was chosen for detailed study. Palaeomagnetic stratigraphy has been used to produce a reliable age model for Baltic Sea cores (Kotilainen *et al*., 2000); this was not possible, however, for post-Ancylus sediments in core 20001-5 (A. Roberts, personal communication), and only one ^{14}C-AMS date has been obtained from this core (U. Struck, personal communication). Varve thickness data is, therefore, the only available measurement of the annual sedimentation rate. The mean sedimentation rate measured from 160 varves in upper sections of the core (Burke *et al*., 2002) is 0.7 mm/yr, which is at the upper end of the normal range of sedimentation rates reported in Gotland Deep cores (0.23–0.75 mm/yr; Christiansen and Kunzendorf, 1998). Only 45 varves, however, were observed in the 165–216 cm interval and indicate a mean sedimentation rate of 0.99 mm/yr $\pm$ 36% ($\pm 1\ \sigma$), similar to the highest sedimentation rate ever reported for a consolidated Gotland Deep core of 1 mm/yr (Ignatius, 1958). This sedimentation rate would imply a time period of 501 yr $\pm$ 36% for the whole 165–216 cm interval. The main problem encountered when applying the mean varve thickness as an estimate of sedimentation rate is that varves are not continuous throughout the 165–216 cm interval. In fact, only 9% of the interval is comprised of varves; therefore, the mean varve thickness may not be representative of these sediments as a whole. Consequently, this study will generally concentrate on the 165–216 cm Mn-record in terms of depth-scale relationships, and the 0.99 mm/yr varve sedimentation rate will only be applied tentatively where appropriate.

Variation in sedimentary Mn-enrichment following saline inflows

To utilize Mn-enrichment records as a proxy for inflow events, the chain of events linking deep-water renewal and the production of a sedimentary Mn-enrichment must be considered.

Renewal by saline inflow is regarded as the only process in which significant changes in Gotland Deep redox conditions occur (Matthäus, 1995), and between inflow events the basin will quickly stagnate (Matthäus and Lass, 1995; Matthäus *et al*., 1996; Nehring *et al*., 1995a; 1995b) producing sulphidic bottom waters in which Mn^{2+} can start to accumulate (Manheim, 1961). Large quantities of Mn^{2+} must accumulate in the deep waters so that a sufficiently large Mn-oxide lamina forms following the next saline inflow event. The formation of Ca-rhodochrosite requires large amounts of free Mn^{2+} to be produced at the sediment-water interface, and it is not known if enough Mn can be supplied to the deep basin by normal sedimentation in one year or less. Ca-rhodochrosite laminae are, however, observed in several successive varves (Burke *et al*., 2002; Burke and Kemp, 2002), indicating that supply of Mn is not normally limiting. The ultimate source of Mn for the Gotland Deep is as Mn-oxides supplied by terrigenous sedimentation (Gingele and Leipe, 1997), but readily reducible Mn-oxides also accumulate on the upper slopes of the Gotland Deep due to cycling of Mn at the redoxcline (Manheim, 1961; Boström and Ingri, 1988). Following the 1994 saline inflow event the redoxcline was elevated by more than 20 m (Matthäus, 1995), and under such circumstances Mn-oxide deposited on the rim of the Gotland Deep may be prone to remobilization through contact with sulphidic waters. In addition some Mn^{2+} will also be liberated by diffusion from the anoxic sediments during stagnation periods.

The 1993–94 saline inflow marked the end of the longest stagnation period (11 yr) recorded in the Gotland Deep since records began in 1880 (Matthäus and Lass, 1995), and prior to this saline inflow the bottom waters also contained the highest concentration of HS^-, Mn^{2+} and Fe^{2+} ever recorded (Brügmann *et al.*, 1997; Heiser *et al.*, 2001). The 1993–94 saline inflow was moderate in terms of volume (Matthäus and Franck, 1992), and, due to mixing in the Baltic's deep basins, the oxygen content of this saline inflow was significantly reduced (Matthäus and Lass, 1995) before entering the Gotland Deep. Nevertheless, in May 1994, Gotland Deep bottom waters were oxygenated (Nehring *et al.*, 1995a), and all of the free Mn^{2+} and Fe^{2+} was oxidized and deposited as a Mn-Fe-oxide lamina (Brügmann *et al.*, 1997). Evidence from the 1993–94 inflow event, therefore, seems to indicate that the supply of oxygen by saline inflows is usually sufficient, even after long stagnation periods, to oxidize all the reduced species accumulated in Gotland Deep bottom waters. One apparent problem of this effect (in terms of Mn-enrichment) is the case where two inflows occur together with no intervening stagnation period; because no reduced Mn^{2+} will exist in the Gotland Deep, the second inflow event may not be recorded by a separate Mn-deposition event.

Mn-oxides are not stable under reducing conditions (Froelich *et al.*, 1979) and, therefore, to produce sedimentary Mn-enrichments the conversion to early diagenetic minerals, such as Ca-rhodochrosite (Huckriede and Meischner, 1996; Sohlenius, 1996; Neumann *et al.*, 1997; Sternbeck and Sohlenius, 1997), and/or Mn-sulphide (Böttcher and Huckriede, 1997; Burke and Kemp, 2002) must occur. Lepland and Stevens (1998) argue convincingly that some Mn^{2+} will be lost at this stage by simply diffusing away into the bottom waters. The overall proportion of the Mn-oxide lamina converted to diagenetic minerals is most likely to depend on the rate of Mn-reduction. More rapid Mn-reduction will cause greater *in situ* Mn^{2+} concentrations and more rapid diagenetic mineral formation and will limit the amount of Mn^{2+} which is lost back into the bottom waters.

Once sedimentary Mn-enrichments are sequestered, they are then subject to burial and the possibility of later diagenesis at depth that may lead to the dissolution of early formed Mn-minerals. Gotland Deep porewaters are often reported to be oversaturated with respect to Ca-rhodochrosite and undersaturated with respect to Mn-sulphide (Heiser *et al.*, 2001; Kulik *et al.*, 2000). Any early-formed Mn-sulphide may dissociate into the porewaters, and not be retained in the record. Jakobsen and Postma (1989) have also observed that Ca-rhodochrosite crystallites are heavily affected by dissolution textures, indicating that within the sediments there may be some dissolution of Ca-rhodochrosite. Gotland Deep sediments are also prone to erosion caused by the inflow events themselves (Heiser *et al.*, 2001; Emeis *et al.*, 1998; Sivkov *et al.*, 1998; Sviridov *et al.*, 1997). Thus, even if Mn-enrichments are sequestered in Gotland Deep sediments, subsequent inflow events can result in the resuspension of Mn-minerals and the removal of evidence of these events from the record. One other factor that must be borne in mind is the possible loss by laboratory handling. Suess (1979) reports that Mn-sulphide crystals can be affected by oxidation when sampled; indeed, an entire sediment slab is reported to have no Ca-rhodochrosite laminae present after exposure to oxygen in transit (Burke *et al.*, 2002).

Conceptual treatment of Mn-record: analysis of a series of events

The many interdependent factors affecting the sedimentary Mn-enrichment outlined above are unlikely to result in a systematic or predictable variance in Mn-enrichment, relating to the strength of an external forcing mechanism for saline inflows, such as the NAO (Hänninen and Vuorinen, 2000). The observed variation in the magnitude of individual Mn-enrichments may, therefore, be effectively independent from any actual variation in the magnitude saline inflow events and the Mn-record may tend to underestimate saline inflow occurrence due to the conditions for depositing and preserving a Mn-enrichment not being met. Nevertheless, the presence of Mn-rich laminae does record the occurrence of past saline inflow events, and the Mn-record (Figure 4) will now be interpreted in terms of a series of events.

Converting the record to a binary signal (0,1,0 . . . n) based on the presence or absence of a Ca-rhodochrosite lamina will allow analysis of the distribution of Mn-enrichments as a series of discrete events (Cox and Lewis, 1966). The Mn-record was resampled every millimetre by two different techniques to produce the two slightly different 'barcode'-type records as shown in Figure 4. The Mn-event (EDS) record was produced by subtracting the mean Mn (wt%) level from the Mn (wt%) record and designating each millimetre with a remaining positive enrichment as a Mn-event (1); negative enrichments were designated as not Mn-events (0). The second Mn-event (visual log) record was produced by considering each millimetre in $\times 5$ BSE images and designating those with visible Ca-rhodochrosite laminae as Mn-events (1) and those without as not Mn-events (0). A section where Mn-sulphide laminae occur (165–171 cm) was excluded from these records as Mn-sulphide laminae are much thicker (~ 3 mm) than Ca-rhodochrosite laminae (~ 0.5 mm), and therefore may relate to more than one saline inflow event.

The EDS and visual log records (Figure 4) ideally should be identical, but in fact differences do occur between the two logs due to the different measurements involved. EDS logs will tend to overestimate the total number of events due to Ca-rhodochrosite laminae straddling sample intervals being recorded as two separate events. The visual log, in contrast, will tend to underestimate the number of events where Ca-rhodochrosite crystallites occur as indistinct concentrations and not as clearly visible laminae. Figure 5A shows a cumulative log of Mn-events, where each step represents a single Mn-event and the slope of the graph is related to the rate of Mn-event occurrence. The EDS log records 134 Mn-events, as compared to 115 Mn-events that occur in the visual log. Figure 5B shows that there is actually little difference between the EDS and visual logs in terms of the distribution of Mn-events occurring in successive 20 mm intervals. Both Figures 5A and 5B clearly show a long-term trend in the data with relatively fewer events occurring towards the top of the 171–219 cm interval.

The bioturbation index (Figure 4) can be used in this setting as a proxy of the mean redox state of specific intervals. Each 20 mm interval can, therefore, be defined in terms of either an oxic or anoxic mean redox state (Figure 5B), allowing the examination of the distribution of Mn-events in terms of the mean redox state in the Gotland Deep, as shown in Table 1. In both EDS and visual logs there are slightly more

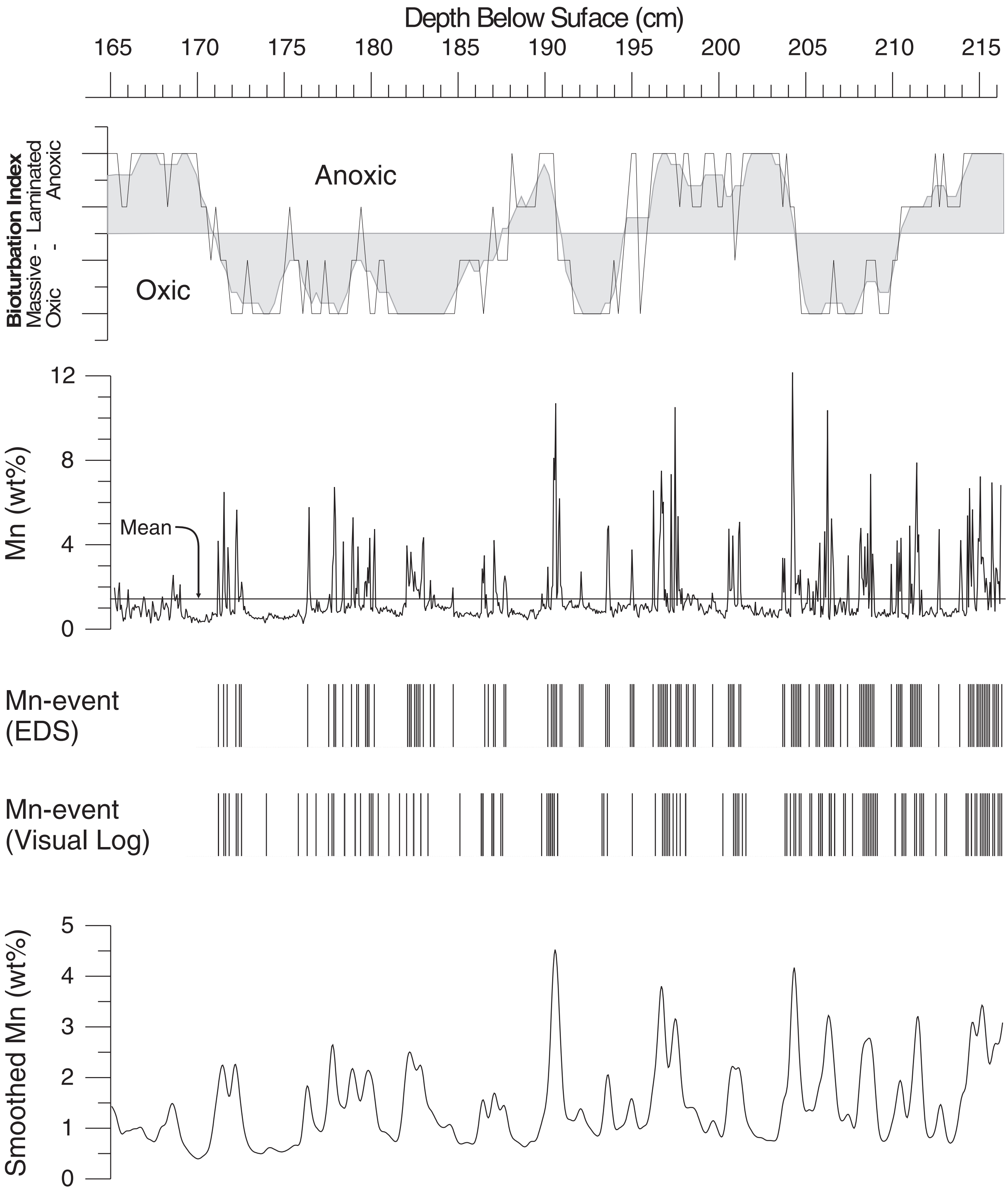

Figure 4 Mn-records, EDS line raster profiles of 51 cm interval (165–216 cm), showing (from top to bottom): bioturbation index profile and Mn (wt%) record, plotted with binary 'barcode' logs of Mn-events from both EDS and visual logging techniques, and a smoothed Mn (wt%) record.

(~11–20%) Mn-events/cm recorded in the anoxic intervals. This is most likely to be due to variations in the geochemical conditions prevailing in the Gotland Deep when individual inflow events occur. In anoxic intervals, the prevailing conditions will generally be sulphidic with bottom water enriched in Mn^{2+}, the vital precursor for sedimentary Mn-enrichment following saline inflow events. The opposite will occur in oxic intervals, thus the number of saline inflows will be more completely recorded in anoxic intervals and less so in oxic intervals. The difference in numbers of Mn-events/cm that occur, between anoxic and oxic intervals, is actually quite small (~11–20%). This indicates that a relatively small difference in the frequency of bottom-water renewal has lead to the quite large changes observed in the bioturbation index and subsequent classification of intervals as either anoxic or oxic.

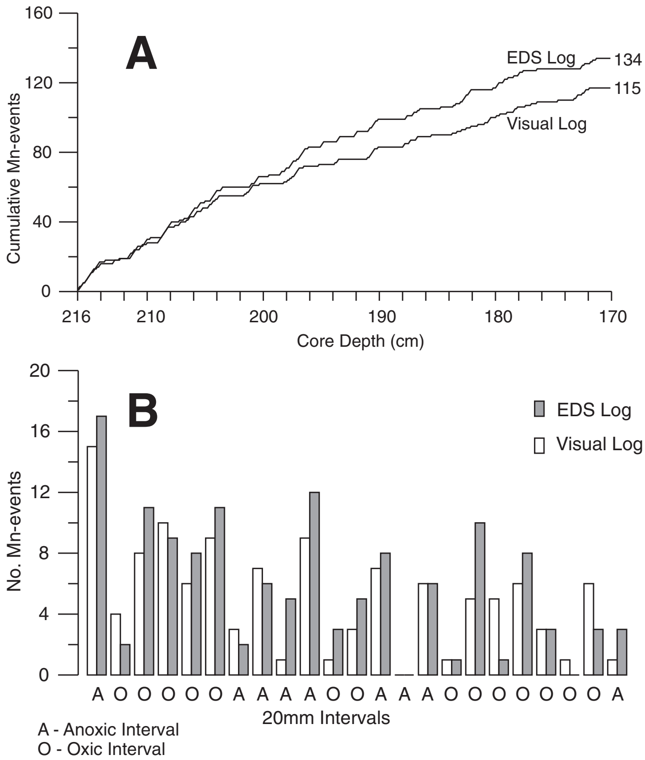

Figure 5 (A) Plot of cumulative Mn-events with depth. (B) Bar chart of number of Mn-events in successive 20 mm intervals (20 mm is the shortest section for which anoxic/oxic intervals can be delineated from the bioturbation record in Figure 4).

The distribution of the intervals between successive Mn-events (i.e., the recurrence interval) will now be considered in comparison to a random distribution of events. Figure 6 summarizes the distribution of Mn-event recurrence intervals, logged by both EDS and visual techniques, as probability density (i.e., the percentage of recurrences at any given interval). Also plotted on Figure 6 is a probability distribution given by the Poisson function. The Poisson distribution is an empirical function that has been applied to describe many random processes, e.g., radioactive decay (Cox and Lewis, 1966). For events that occur randomly and independently, with a number of successes (×), with a constant rate (μ) per unit time or region, the probability distribution f(×) is given by the following equation (× = 0,1,2 . . . n):

$$f(\times) = p(\times;\mu) = \frac{e^{-}\mu^{\times}}{\times!}$$

The Poisson distribution provides a good approximation of Binomial distribution (and Normal distribution at high μ) but has the advantage of being set by just one external variable

Table 1 Distribution of Mn-events between oxic-anoxic intervals

	No. Mn-events	Total depth of intervals (cm)	Mn-events/cm	Range (as % of total)
EDS Log				
Oxic Int.	75	28	2.7	
Anoxic Int.	59	18	3.3	
Total Int.	*134*	*46*	*2.9*	20.6
Visual Log				
Oxic Int.	68	28	2.4	
Anoxic Int.	49	18	2.7	
Total Int.	*117*	*46*	*2.5*	11.5

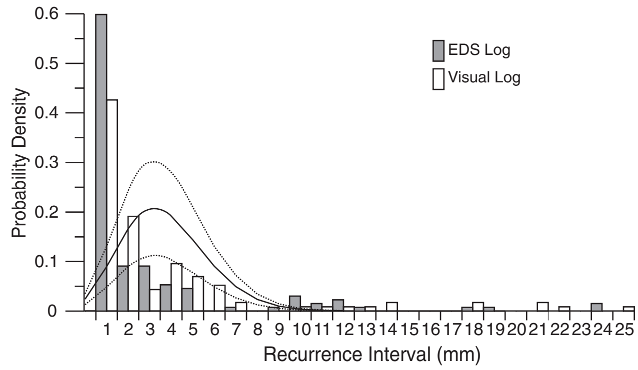

Figure 6 Bar chart of probability density of Mn-event recurrence intervals, with a line plot of a Poisson distribution (mean = 3.75, ±2 σ error limits).

μ (Kreyszig, 1999). In the specific case of Mn-event recurrence intervals considered here, if × = the actual recurrence interval, then μ = average number of successes in a given time or region, i.e., the mean recurrence interval. The mean recurrence interval for Mn-events is 3.43 mm (EDS) and 3.93 mm (visual), respectively; therefore, an intermediate μ-value of 3.75 mm has been used to set the Poisson distribution in Figure 6. Error limits have also been added at 2 σ above and below the ideal Poisson distribution. Derivation of 2σ is from observations of 100 random data sets of 120 events produced by a Poisson function embedded in an internet Java-applet (www.math.uah.edu/stat/applets/PoissonExperiment.html). If the Mn-event recurrence interval probability density distribution were also observed to be within these 2 σ error limits, then it would be very likely that the occurrence of Mn-events is simply a random stochastic process, with no long-range order. It is quite clear from Figure 6, however, that this is not the case. Both Mn-event distributions are highly skewed towards short recurrence intervals with over 0.6 (60%) of the recurrence intervals at 1 or 2 mm. There are conversely low numbers of recurrence intervals of between 3 and 8 mm, but also a long tail of recurrence intervals over 10 mm. The Mn-event records are, therefore, characterized by groups of successive Mn-events interrupted by longer intervals without Mn-events. It is also likely that this distribution of Mn-events (and the inflow-events that cause them) is, therefore, not random and indeed may be forced by an external mechanism, producing periods of high Mn-event occurrence and interim periods of low Mn-event occurrence.

Spectral analysis

As discussed above, interannual-scale variability in Gotland Deep conditions can lead to large variations in the amount of Mn sequestered in the sediments on millimetre scales. Despite this variation, there is possibly longer-term order with respect to the presence or absence of groups of inflows. Sufficient smoothing of the raw Mn (wt%) data (Figure 4) will, therefore, produce a depth averaged record in which groups of saline inflows should lead to broad intervals of Mn-enrichment, suitable for analysis in terms of centimetre (possibly decadal) scale variance. In preparation for spectral analysis, a smoothed Mn-series (Figure 4) was produced by application of a 5 mm gaussian K-smooth filter.

The linear trend, and the data mean, were removed from the Mn-series prior to spectral analysis, and two different techniques were then applied to the smoothed Mn-series in order to produce spectral estimates, using AnalySeries v1.2 (Paillard *et al.*, 1996). Figure 7A shows a spectral estimate produced by

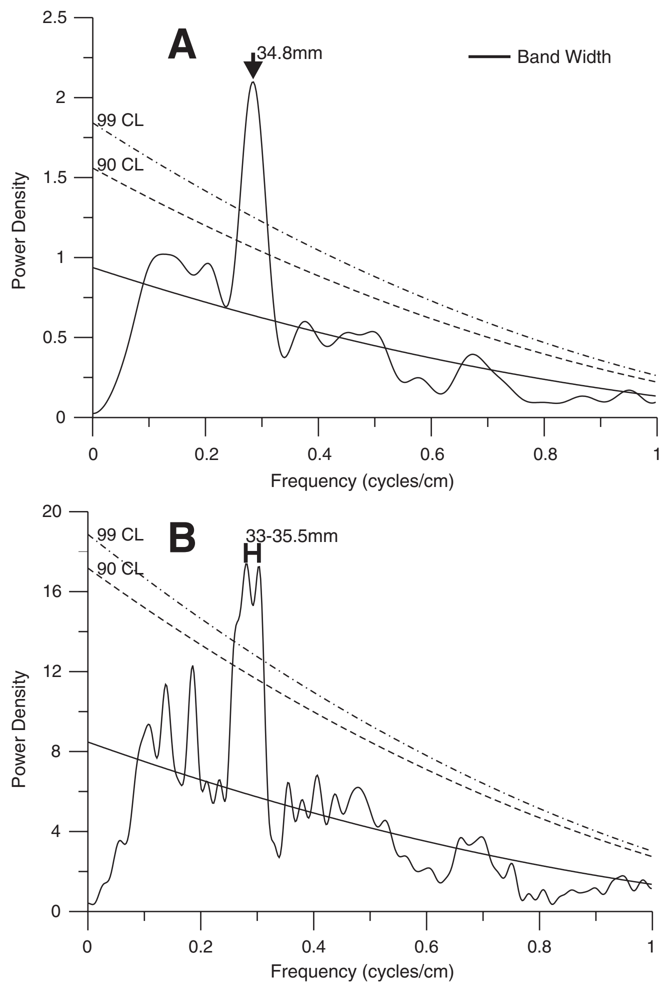

Figure 7 (A) Spectrum of smoothed Mn (wt%) series from the Blackman-Tukey method. (B) Spectrum of smoothed Mn (wt%) series from the multi-taper method.

the Blackman-Tukey method (BTM) (first introduced by Blackman and Tukey, 1958, and developed by Jenkins and Watts, 1968) by application of 362 lags of a single Tukey window. Figure 7B shows a spectral estimate produced by the multi-taper method (MTM; Thomson, 1982), by application of three eigentapers. Background spectra were added to both spectral estimates by applying a second-order polynomial quadratic least squares fit to estimate the background 'red noise' spectrum found in many natural time series (Ghil and Yiou, 1995; Thomson, 1990). Upper significance intervals were then added to the polynomial fits by application of a chi-squared distribution with two (BTM) and six (MTM) degrees of freedom (DOF), respectively (Dettinger *et al*., 1995, state that the number of DOF = 2 K; where K = number of spectral windows/tapers applied). BTM produces spectral estimates with moderate spectral resolution and significance intervals, whereas MTM produces better spectral resolution but with poorer significance intervals. While Thomson (1990) argues that only the MTM produces reliable spectral estimates, Paillard *et al*. (1996) advise a common-sense approach where spectra from more than one technique are considered when interpreting significant frequencies. The BTM spectra show a significant peak at 34.8 mm, which is resolved as two subpeaks at 33 and 35.5 mm in the MTM spectra, indicating at least one significant periodicity present in the smoothed Mn-records between 33 and 35.5 mm.

The sedimentation rate in this 51 cm section is not well constrained (see above); however, applying the range of measured varve thickness for this section (0.99 mm ± 36%) does indicate a plausible range for this discrete decadal periodicity, placing it somewhere between 25 and 55 years. This periodicity in Mn-events is likely not to completely reflect the saline inflow events, due to the incomplete translation to Mn-enrichments. Neumann *et al*. (1997), however, have also reported sedimentary Mn-enrichments in a well-dated (^{210}Pb) Gotland Deep core with maxima every 30–60 years that are consistent with historical clusters of saline inflows. There seems to be some consistency between the Mn-records discussed in this study and in Neumann *et al*. (1997). This consistency does not extend to the periodicities reported for the instrumental NAO index records, which have weak (not statistically significant) frequency maxima at 2, 7–8, 20 and 70 yrs (Hurrell and van Loon, 1997), missing out the periodicity range indicated by both Mn-records. Thus there appears to be an inconsistency between the reports that indicate that North Atlantic climatic variations (NAO) ultimately drive the variations in saline inflow to the Baltic Sea (above) and the records of Mn-events from Gotland Deep sediments which record these same inflow events.

This inconsistency is a common problem for all reported proxy records of North Atlantic climate. Spectral analysis of ice accumulation rates in Greenland ice cores have revealed a prominent 90-year periodicity (Appenzeller *et al*., 1998), and comparison of ice-core, tree-ring and instrumental records of NAO (see Schmutz *et al*., 2000, and references therein) have shown that proxy records have only modest reconstructive skill at decadal timescales, and no skill at interannual timescales. Schmutz *et al*. (2000) do indicate, however, that in future studies a combination of different proxy records (e.g., Cullen *et al*., 2001) could significantly improve reconstructive ability. Further Mn-records from well-dated Holocene Gotland Deep cores are, therefore, now needed to confirm the natural variation present in Gotland Deep sediments, both to improve understanding of Baltic Sea processes and to provide much-needed records which may aid in the understanding of North Atlantic climate processes.

Conclusions

Use of SEM-based techniques has allowed the high-resolution measurement of sedimentary Mn-enrichments, potentially providing an interannual-scale record of saline inflows to the Baltic Sea.

On decadal timescales, suitably smoothed Mn-enrichment time series do provide a good record of the longer-term variance in saline inflows, in terms of the presence or absence of groups of inflows. A significant spectral peak has been observed in the smoothed Mn-record at 33–35.5 mm, which may relate to periodic variance in saline inflow occurrence during the mid-Holocene on multidecadal timescales.

Although groups of inflows are recorded by an increase in Mn (wt%) enrichments on decadal timescales, at the lamina scale individual saline inflow events may not be recorded or may be removed from the record by dissolution or erosion, leading to the under-recording of events. Mn-records are, therefore, unlikely to provide valid records of interannual-scale variation in saline inflows.

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