Pelagic molybdenum concentration anomalies and the impact of sediment resuspension on the molybdenum budget in two tidal systems of the North Sea

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Abstract

The seasonal dynamics of molybdenum (Mo) were studied in the water column of two tidal basins of the German Wadden Sea (Sylt-Rømø and Spiekeroog) between 2007 and 2011. In contrast to its conservative behaviour in the open ocean, both, losses of more than 50% of the usual concentration level of Mo in seawater and enrichments up to 20% were observed repeatedly in the water column of the study areas. During early summer, Mo removal by adsorption on algae-derived organic matter (e.g. after *Phaeocystis* blooms) is postulated to be a possible mechanism. Mo bound to organic aggregates is likely transferred to the surface sediment where microbial decomposition enriches Mo in the pore water. First $\delta^{98/95}\text{Mo}$ data of the study area disclose residual Mo in the open water column being isotopically heavier than MOMo (Mean Ocean Molybdenum) during a negative Mo concentration anomaly, whereas suspended particulate matter shows distinctly lighter values. Based on field

observations a Mo isotope enrichment factor of $\epsilon = -0.3\text{‰}$ has been determined which was used to argue against sorption on metal oxide surfaces. It is suggested here that isotope fractionation is caused by biological activity and association to organic matter.

Pelagic Mo concentration anomalies exceeding the theoretical salinity-based concentration level, on the other hand, cannot be explained by replenishment via North Sea waters alone and require a supply of excess Mo. Laboratory experiments with natural anoxic tidal flat sediments and modelled sediment displacement during storm events suggest fast and effective Mo release during the resuspension of anoxic sediments in oxic seawater as an important process for a recycling of sedimentary sulphide bound Mo into the water column.

Keywords

Molybdenum, Mo isotopes, *Phaeocystis* sp., sediment resuspension, storm events, tidal flats, German Wadden Sea, North Sea

1. Introduction

Molybdenum (Mo) is a redox-sensitive trace metal occurring as dissolved molybdate (MoO_4^{2-}) in the oxygenated ocean with a concentration of about 110 nM (Morris, 1975; Collier, 1985). Although Mo is involved in biological cycles, its behaviour is generally considered to be conservative (e.g. Howard and Cole, 1985; Cole, 1993). An increasing number of recent studies, however, demonstrate temporal deviations from conservative behaviour in different aquatic ecosystems. Mo removal from oxic seawater can be caused by various processes, e.g., scavenging by freshly formed manganese oxides, Fe-oxyhydroxides, organic matter, and assimilation by phytoplankton (e.g. Szilagyi, 1967; Head and Burton, 1970; Berrang and Grill, 1974; Nissenbaum and Swaine, 1975; Yamazaki and Gohda, 1990; Cole, 1993; Tuit and Ravizza, 2003). Substantial temporary Mo depletion in coastal and offshore waters was first observed by Dellwig et al. (2007) who suggested Mo fixation in oxygen-depleted microzones of aggregated suspended matter and/or adsorption to freshly formed organic matter.

In sulphidic environments MoO_4^{2-} is transformed to particle-reactive thiomolybdates (Erickson and Helz, 2000) until final burial as MoS_2 . Furthermore, Mo can be incorporated into Fe sulphides or bound to organic matter (e.g. Huerta-Diaz and Morse, 1992; Helz et al., 2004; Vorlicek et al., 2004; Helz et al., 2011). In addition, substantial adsorption of Mo on the surfaces of Mn and Fe oxi(hydroxi)des has been found (e.g., Berrang & Grill, 1974) which

may lead to a cycling between the oxic and suboxic zones of aquatic and sedimentary systems when these species are oxidized or reduced.

In permeable sediments influenced by advective pore water transport, Mo attached to metal oxides can be transported into anoxic sediment layers (Boudreau and Jørgensen, 2001; Rusch and Huettel, 2000) and may be released when the metal oxides are reduced by H₂S (Adelson et al., 2001). Complexation by dissolved organic compounds has been suggested to cause stabilisation of dissolved Mo (Brumsack and Gieskes, 1983) which may retard the fixation in anoxic sediments thereby allowing again the release into the overlying water column (Dellwig et al., 2007; Beck et al., 2008; Kowalski et al., 2009).

Mo isotope fractionation is known to occur when Mo is removed from the aqueous solution during fixation by different solid interfaces under anoxic and oxic conditions (e.g., Barling and Anbar, 2004; Arnold et al., 2004; Nägler et al., 2005; Goldberg et al., 2009, 2012). Thus, Mo isotopes are a useful tool to identify the processes involved in Mo partitioning between water column and sediment. While the scavenging of Mo by Mn oxides is suggested to result in light isotope signatures (Barling et al., 2001; Siebert et al., 2003; Poulson et al., 2006; Wasylenki et al., 2008; Goldberg et al., 2012), more effective removal of Mo from solution under euxinic conditions leads to smaller to negligible isotope fractionation depending on the sulphide level (e.g. McManus et al., 2002; Arnold et al., 2004; Neubert et al., 2008; Nägler et al., 2011).

Reoxidation of sedimentary sulphidic compounds may take place during e.g. extensive sediment displacement (Aller et al., 1986) or bioturbation (Boudreau and Jørgensen, 2001; Volkenborn et al., 2007) and may result in a significant release of trace metals like Mo. A partial reoxidation can be also caused by advective circulation of oxygenated waters through the top sediments which enhances O₂ penetration into permeable sediments (de Beer et al., 2005).

Large scale sediment erosion and resuspension of tidal flat sediments is caused by tide- and wind-driven wave activity (e.g. de Jonge and van Beusekom, 1995; You, 2005; Stanev et al., 2006; Christiansen et al., 2006; Bartholomä et al., 2009; Fettweis et al., 2007, 2010). Pronounced sediment transport may in particular take place during storm events. Such resuspension processes also cause remobilisation and transfer of trace metals into the water column (e.g., Cantwell et al., 2002; Saulnier and Mucci, 2000; Audry et al., 2006, 2007; Kalnejais et al., 2007, 2010) finally altering the geochemical signature of the open water column. The extent of the impact will depend on the reservoir sizes and the residence time of sedimentary compounds under oxic conditions (Morse, 1994; Saulnier and Mucci, 2000).

With the help of modelling approaches, the residence times and fluxes of suspended particulate matter in the water column during storm conditions can be estimated (e.g. Warner et al., 2008; Lettmann et al., 2009; Gräwe and Wolff, 2010; Dobrynin et al., 2010).

In this contribution, we investigate the seasonal dynamics of Mo in two tidal systems of the German Wadden Sea with different sedimentological and hydrodynamic properties. Possible mechanisms for non-conservative behaviour of Mo as expressed by temporary negative and positive concentration anomalies in the water column are discussed. In this context, the oxidative release of Mo from the sediments during resuspension is examined by experimental and modelling approaches estimating the potential consequences for the Mo inventory in the water column. Furthermore, we present first Mo isotope data from the coastal area of the North Sea, which provide complementary information about the geochemical behaviour of Mo.

2. Study areas

The Wadden Sea is about 450 km long stretching from Den Helder in the Netherlands to Blåvandshuk in Denmark along the southern North Sea coastline (Streif, 1990). Sampling was carried out in the backbarrier tidal flats of the Islands of Spiekeroog in the southern part of the German Wadden Sea and in the backbarrier tidal flats of the Islands Sylt and Rømø in the northern part (Fig. 1).

The backbarrier tidal area of Spiekeroog Island (Fig. 1A) covers an area of about 74 km² (Walther, 1972) and water exchange with the open North Sea occurs via the tidal inlet (Otzumer Balje, OB) between the Islands of Langeoog and Spiekeroog. Tides are semi-diurnal with a mean range of 2.6 m (Flemming and Davis, 1994). The backbarrier area is dominated by sand and mixed flat sediments with grain sizes decreasing towards the mainland due to lower current velocities (e.g. Postma, 1961; Reineck et al., 1986; Flemming and Nyandwi, 1994).

The Sylt-Rømø tidal basin (Fig. 1B) is a semi-enclosed bight encompassing an area of about 407 km² and is characterised by semi-diurnal tides with a mean range of about 2 m. Tidal water transport occurs via a single tidal inlet branching into three main tidal channels (Gätje and Reise, 1998). Most of the sediment consists of mixed sand and sandy sediments whilst fine sediments prevail along the fringes (Bayerl et al., 1998).

3. Material and Methods

3.1. Sampling

Water and suspended particulate matter (SPM) samples were taken aboard R/V “Navicula” close to a time series station in the tidal inlet of site Spiekeroog (site OB, Fig. 1A, 53°45.0'N, 7°40.3'E; water depth ca. 13 metres, Grunwald et al., 2007). At Sylt Site, sampling was carried out in the tidal channel called Lister Ley (LL, Fig. 1B, 55°01.30' N, 8°27.10' E, water depth ca. 10 metres) using R/V “Mya”.

For SPM, 0.5 to 1 L seawater was filtered through pre-weighted polycarbonate filters (Millipore Isopore membrane filters, 0.4 µm pore size, low-pressure max -20 kPa). Afterwards the filters were rinsed with 100 mL purified water and dried for 48 h at 60° C. For algae cells counts, water samples were fixed with Lugols solution and stored in amber glass bottles at 4°C.

Seawater samples were filtered through 0.45 µm SFCA (surfactant-free cellulose acetate) syringe filters and acidified to 1% (v/v) with concentrated HNO₃ (supra pure, Merck).

Surface sediment samples were taken with cut plastic 60 ccm syringes, placed into 60 ccm plastic centrifuge tubes, and, after return to the laboratory, kept frozen until freeze-drying and further analysis as described by Neubert et al. (2008).

3.2. Analytical methods

At site Spiekeroog, temperature was determined as a mean of ten minutes intervals at the time series station (OB). Salinity was calculated from temperature, conductivity and hydrostatic pressure (UNESCO, 1985). In the Sylt area, temperature was measured with an electronic reversing thermometer (SiS, Sensoren Instrumente Systeme GmbH) which was mounted on a niskin bottle. Salinity was measured with a salinometer (Guildline Instruments, Autosal 8400).

For analysis of Mo in suspended particulate matter (SPM) the polycarbonate filters were digested with a mixture of HNO₃, HClO₄, and HF using a pressure digestion system PDS-6 (Loftfields Analytical Solutions; Heinrichs et al., 1986) at 180°C for 6h and were measured by ICP-OES (Thermo, iCAP 6300 Duo). A detailed description of the digestion method, which was also used for sediment samples, is given by Dellwig et al. (2007). Accuracy and precision of the analyses were determined by simultaneous measurements of the certified reference standard SGR-1 (green river shale, United States Geological Survey) and were better than 7.3% and 5.6%, respectively.

Dissolved Mo and Mn in seawater samples were measured by ICP-OES (Thermo, iCAP 6300 Duo) and HR-ICP-MS (Element II, Thermo Fisher Scientific) using 2-fold and 10-fold diluted aliquots, respectively. Accuracy and precision were determined with the certified seawater standard CASS-4 (National Research Council of Canada) and were better than 7.5% and 6.5%, respectively.

Taxa determination and cell counting was performed using an inverted microscope following the Utermöhl method (Utermöhl 1931, Lund et al. 1958). Phytoplankton cell dimensions were measured for up to 25 cells of every taxon that occurred at the respective sampling date. Cell volumes were calculated according to the geometric shapes proposed by Hillebrand et al. (1999).

For $\delta^{98/95}\text{Mo}$ measurements 100 ml water were spiked with a ^{97}Mo and ^{100}Mo double-spike. After evaporation, the samples were redissolved in 4 M HCL with trace H_2O_2 . Mo purification applying anion and cation exchange columns followed Neubert et al. (2011). The isotopic composition of Mo was measured with a Nu instruments MC-ICP-MS. A detailed description of the analytical technique is given by Siebert et al. (2001) and Wille et al. (2007). A minimum of 20 ng Mo was used per analyses. Analytical blanks (<2 ng) were small compared to the typical total amount of sample Mo processed (<1.5%). For isotope data presentation the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio was used. The standard reproducibility was better than 0.06‰ (2 σ). Isotope composition was presented as ‰ deviation from Johnson Matthey ICP standard solution (lot 602332B, Siebert et al., 2001):

$$\delta^{98/95}\text{Mo} = [(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}} / (^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}} - 1] * 10^3 \quad [1].$$

The $\delta^{98/95}\text{Mo}$ of NIST SRM 3134 is 0.25‰ relative to this standard, and ocean water (Mean Ocean Molybdenum, MOMo) is 2.34 ± 0.07 ‰ (Greber et al 2012).

3.3. Oxidation experiment

A laboratory experiment with natural anoxic tidal flat sediments was conducted to investigate the liberation of Mo during mixing with oxygenated seawater. After removal of the thin oxic surface layer (1-5 mm), the first 10 cm of anoxic sediment material were collected in March 2008 from a sand flat (Fig. 1A, Janssand JS, 53°44.18' N, 7°41.90' E, mud fraction <5%) and a mixed flat site (Fig. 1A, NN, Neuharlingersieler Nacken, 53°42.15' N, 7°42.57' E, mud fraction about 15%) to consider the dominant sediment types of the study area (e.g., Flemming and Ziegler, 1995; Al-Raei et al., 2009). In the laboratory, the sediments

were sub-sampled in a glove bag under N₂ atmosphere (Sigma-Aldrich, Milwaukee, USA) to avoid O₂ contamination. For metal analysis of the original material, samples were taken from both sediment types and stored frozen in plastic petri dishes until analyses. For the experiment about 1 kg of the sediment material was filled into plexiglass tubes (length 45 cm, diameter 5 cm) closed with rubber plugs. The experiment started with the addition of 0.5 L oxygenated artificial sea water containing no Mo. The tubes were agitated continuously during the entire experiment duration of 6 h using a shaking bed (Gerhardt Analytical systems, Königswinter, Germany) to ensure homogenous resuspension of the sediment material. Aliquots of 2 mL were taken from the water column every 15 min with a 5 mL syringe for the analysis of dissolved Mo released during oxidation. Based on pore water Mo concentrations and the water content of the used sediment, a possible interference of pore water Mo can be excluded. Immediately after sampling the aliquots were filtered through 0.45 µm SFCA syringe filters and acidified to 1% (v/v) with concentrated HNO₃. The solutions were analysed by ICP-OES as described above.

3.4. Estimating SPM residence times with a Lagrangian particle tracking model

A Lagrangian particle tracking model (Gräwe and Wolff, 2010) was used to simulate short-term SPM dynamics and particle residence time in the water column of the backbarrier area of Spiekeroog Island using the conditions during the storm event “Britta” (31 October - 2 November 2006). On that account, the Lagrangian SPM module was adapted to a hydrodynamic core model (GETM, General Estuarine Transport Model, Burchard and Bolding, 2002) which was coupled to a wave model (SWAN, Simulating Waves Nearshore, Booij et al., 1999). A detailed description and validation of the hydrodynamic model and the Lagrangian particle tracking model can be found in Lettmann et al. (2009) and Gräwe and Wolff (2010).

The model simulated the time period from 20 October to 4 November 2006. To estimate the residence time of particles in the water column the following procedure was used: 1500 particles with a diameter of 50 µm were placed randomly distributed in each 200 x 200 m grid cell (20 million particles in total). The diameter was chosen as a fair estimate for the present grain size spectrum ranging from clayey to sandy material. As soon as the bottom stress of 0.12 N/m² was reached, particles could be resuspended and released into the water column. For bottom stress values below 0.12 N/m² only sedimentation was possible. For a detailed description and validation of the erosion and sedimentation modules the reader is referred to Gräwe and Wolff (2010).

For each particle, the residence time in the water column, i.e., the time from resuspension until deposition, was calculated. Afterwards, a mean value was calculated for all particles in a grid box. This procedure was done over one tidal cycle computing a temporal average over these 12.4 hours (this limits the maximum residence time to 12.4 hours). Thereafter, the particle positions were reset and the simulation was started again with a time shift of 2 hours until the final simulation time was reached.

4. Results and discussion

4.1. Negative concentration anomalies of dissolved Mo

Distinct deviations of dissolved molybdenum (Mo_{diss}) from salinity-based theoretical values appeared repeatedly in the water column of Site Spiekeroog (OB) during certain time periods between 2007 and 2010 (Fig. 2a). In comparison to previous studies (Dellwig et al., 2007; Kowalski et al., 2009), the time-series presented in this contribution revealed significant fluctuations of Mo_{diss} throughout the years due to a higher sampling resolution over an extended time period. During early summer Mo_{diss} decreased temporarily down to a minimum value of 50 nM representing less than 50% of the salinity-based Mo concentration. Unfortunately, this behaviour could not be shown in 2009 due to lacking samples for the time period between mid-June until the end of August. The negative Mo_{diss} concentration anomaly was also observed at the Sylt Site in 2008, less pronounced in 2010, and again in 2011 (Fig. 3a). This observation allows the conclusion, that Mo depletions are common phenomena in the investigated tidal basins of the North Sea, thus likely appearing within the entire Wadden Sea. The decrease in Mo_{diss} concentrations at the Sylt Site was observed in the years 2008-2010 about four weeks later than at the Spiekeroog Site. This is in line with previous observations (Dellwig et al., 2007) which indicated a development of the Mo_{diss} concentration anomaly from the western to the eastern parts of the East Frisian Wadden Sea.

Several authors reported coupled transport behaviour between Mo and Mn via scavenging of Mo by Mn oxides (e. g., Berrang and Grill, 1974). The time-series of site Spiekeroog in 2007 and 2008 revealed a parallel decrease of Mo_{diss} and Mn_{diss} concentrations which may be a result of elevated photochemical and/or bacterial Mn oxidation (Emerson et al., 1982; Anbar and Holland, 1992; Nico et al., 2002) and subsequent scavenging of Mo. However, observations by Dellwig et al. (2007) and Kowalski et al. (2012) showed that the decreasing Mn_{diss} concentrations in summer were not caused by Mn oxidation but were due to decreasing availability of reactive Mn in the surface sediments.

A comparison with the phytoplankton dynamics (Figures 2b and 3b) implied a connection between the Mo_{diss} depletion and phytoplankton blooms (expressed as cell carbon) in early summer. Although the diatom blooms in spring seemed to have a limited influence on the Mo_{diss} concentrations, pronounced depletions occurred after the *Phaeocystis* blooms. This early summer depletion persisted for the longest period at the Spiekeroog Site in 2008. A significant loss of Mo_{diss} is seen in June followed by a second smaller decline in August which may be attributed to the influence of the *Phaeocystis* bloom in April/May and the less pronounced summer diatom bloom in June/July. At the Sylt Site, the diatom bloom occurred about one month later at the end of March 2008 (Figs. 3b). Similar to the diatoms, *Phaeocystis* sp. also bloomed later in Sylt, which was followed by a significant negative concentration anomaly of Mo_{diss} . These differences in timing of the blooms were probably related to local factors including temperature (e.g. van Beusekom et al., 2009) and light conditions during the previous winter months (e.g. Cadée, 1986). The shorter duration of the Mo depletion near Sylt might be due to the less pronounced *Phaeocystis* bloom ($390 \mu\text{g carbon L}^{-1}$). The importance of the *Phaeocystis* bloom in early summer became especially clear in the time series data of Sylt Site in 2010. Although the diatom bloom in spring lead to exceptionally high cell carbon concentrations, the Mo_{diss} depletion was only weakly expressed as *Phaeocystis* sp. also showed only low abundance. However, the lacking Mo depletion at Sylt Site in 2009, albeit a pronounced *Phaeocystis* bloom was present, remains enigmatic.

The crucial difference between diatom and *Phaeocystis* blooms is the enormous release of organic mucus during breakdown of the latter species (e.g. Schoemann et al., 2005). Although the mucilaginous matrix is not included in the determined cell carbon (Figs. 2b and 3b) a considerable release of excess organic matter to the water column can be assumed which probably traps Mo_{diss} . This assumption is supported by measurements of suspended particulate matter during a Mo depletion period in July 2005 when organic matter contents (max. 29%) corresponded with elevated Mo values (max. 40 mg kg^{-1}) (Dellwig et al., 2007). Furthermore, the proposed relationship between Mo and organic matter is in accordance with a number of studies (Szilagyi, 1967; Head and Burton, 1970; Nissenbaum and Swaine, 1975; Yamazaki and Gohda, 1990; Coveney et al., 1991; Helz et al., 1996; Lyons et al., 2003; Algeo et al., 2007).

The transfer of Mo_{diss} onto SPM was also indicated by $\delta^{98/95}\text{Mo}$ values showing an enrichment of the lighter isotope on SPM whereas the residual Mo_{diss} fraction revealed a heavier isotopic composition finally pointing towards isotopic fractionation and preferential removal of the lighter Mo isotope from the aqueous phase (Table 1, Fig. 4). The net non-

conservative behaviour of dissolved Mo suggests that in a first-order approach the water column can be regarded as a closed system with respect to Mo_{diss} . Therefore, based on the development of the aqueous solution, an enrichment factor was calculated considering a Rayleigh approach:

$$\varepsilon = (\delta^{98/95}\text{Mo} - \delta^{98/95}\text{Mo}_{\text{MOMo}}) / \ln f \quad [2]$$

$$\delta^{98/95}\text{Mo} = \delta^{98/95}\text{Mo}_{\text{MOMo}} + \varepsilon \cdot \ln f \quad [3]$$

with f representing the residual fraction of Mo_{diss} in the water column. Evaluation of the field data yields an enrichment factor ε of -0.3‰ (Fig. 5). Isotope enrichment factors describing the behaviour of Mo isotopes during the interaction between Mo_{diss} and Mn oxides or Fe-oxyhydroxides as well as during the assimilation by microorganisms (soil bacteria, cyanobacteria) have already been established experimentally (Wasylenki et al., 2008; Goldberg et al., 2009; Zerkle et al., 2011). The application of equation (3) using the experimentally derived enrichment factors indicates, that the observed field data cannot be reproduced assuming sorption onto metal (oxyhydr)oxide surfaces as responsible process (Fig. 5). Moreover, the calculated enrichment factor was close to results determined experimentally during active Mo uptake by cyanobacteria (Zerkle et al., 2011). Although cyanobacteria may be important in the sediments of the study area (Evrard et al., 2008), they are not expected to influence the Mo reservoir in the open water column due to negligible abundances and dissolved sulphate at seawater level competing with molybdate for active assimilative uptake (Howarth and Cole, 1985; Cole et al., 1993; Marino et al., 2003). Furthermore, Mo depletion occurred during periods of decreasing phytoplankton abundance and not during the growth period (Fig. 2). Thus, active uptake of Mo by phytoplankton can be ruled out to cause significant Mo_{diss} depletion in early summer. Therefore, it is hypothesised that extracellular Mo-binding to algae-derived organic matter may have caused the observed Mo isotope fractionation, although the actual isotope enrichment factor for Mo adsorption onto organic matter is not known so-far. A more detailed analysis of the processes leading to the observed Mo isotope fractionation effects requires further field and in particular further experimental and modelling studies.

Several studies document adsorption of metal cations onto algal and bacterial cell walls (e.g. Gonçalves et al., 1987; Xue et al., 1988; Fein et al., 1997; Daughney et al., 1998; Seders and Fein, 2011). For instance, Mn is known to be adsorbed to *Phaeocystis* mucus (Davidson

and Marchant, 1987; Schoemann et al., 2005). Phytoplankton releases surface-active exopolymeric substances, supporting the aggregation of organic and inorganic particles (e.g. Passow, 2002a). The increased release of organic matter during and after the breakdown of *Phaeocystis* blooms together with higher water temperatures leads to enhanced microbial activity in early summer (Lemke et al., 2010). The additional release of exudates by bacteria as well as the bacterial modification of phytoplankton-derived substances to transparent exopolymer particles (TEP) by bacteria (Passow, 2002b; Bhaskar et al., 2005) leads to the formation of large aggregates and thus an enhanced flux of organic-rich particles to the sediment surface in the summer months (Riebesell, 1991a, b; Kiørboe et al., 1994; Logan et al., 1995; Simon et al., 2002; Chang et al., 2006; Lunau et al., 2006). Harvey and Leckie (1985) studied the importance of extracellular polysaccharides (EPS) for metal adsorption and found that EPS released by bacteria competes with bacteria cell walls for available metals. Acharya et al. (2009) found anionic uranyl (UO_2^{2+}) being bound to EPS of a marine cyanobacterium. Although less is known about the adsorption of anions (e.g., Fein et al., 2001), Mo_{diss} adsorption to surface-active TEP directly released by *Phaeocystis* sp. as well as organic compounds produced after their blooms is postulated to play a key function in removing Mo_{diss} from the water column in the study area. Such sequence of organic matter production by algae followed by bacterial modification may also explain the time gap between *Phaeocystis* breakdown and Mo depletion (Figs. 2 and 3). In contrast, the less pronounced response of Mo_{diss} dynamics during spring diatom blooms is probably explained by a lower release of organic matter by these species as well as a reduced microbial activity due to lower temperatures (Lemke et al., 2010).

Subsequent aggregation of suspended particles by released organic matter may lead to deposition of organically bound Mo in the sediment (Dellwig et al., 2007). The relatively short time necessary to produce Mo concentration anomalies may be explained by a rapid, event-like sinking and deposition of the large aggregates as it has been reported by e.g. Riebesell (1991a), Alldredge and Gotschalk (1989), and Chang et al. (2006). The transfer of Mo to the surface sediments as well as its release after the decomposition of deposited organic-rich particles is indicated by enrichments of Mo_{diss} in the shallow pore waters of site Spiekeroog partly exceeding the usual seawater value by a factor of four (Dellwig et al., 2007; Beck et al., 2008; Kowalski et al., 2009).

Additionally, the analysis of the periostraca (protective organic coatings) of bivalves found in the sediments of the study area supported the assumption of a tight relation between Mo and organic matter under natural conditions in this environment. While Mo_{part} contents of

the periostracum of *Mytilus edulis* living in colonies above the sediment surface showed values of up to 8 mg kg⁻¹, the burrowing *Ensis americanus* reached contents of up to 256 mg kg⁻¹. The isotopic composition of the latter periostracum resembled those of SPM with a $\delta^{98/95}\text{Mo}$ value of +1.3 ‰ (Table 1) thereby indicating a Mo isotope fractionation between dissolved and organically bound Mo and an enrichment of the lighter isotope in the organic matrix compared to the aqueous solution.

4.2. Positive concentration anomalies of dissolved Mo

Apart from depletion periods, the time series of pelagic Mo_{diss} at both sites also revealed positive Mo concentration anomalies. While the time-series of Mo_{diss} generally showed a slightly enhanced level at Spiekeroog Site in 2009 and at Sylt Site in 2011 most prominent anomalies occurred especially in late summer 2007, 2010 and spring 2008 at Spiekeroog Site and early summer 2009 as well as spring 2011 at Sylt Site. The enrichments were about 20 nM above the theoretical salinity-based Mo_{diss} values (Mo_{sal} ; Figs 2a and 3a) and thus significantly above the analytical error (compare Chapter 3.2). Enhanced Mo_{diss} concentrations in spring may be caused by the release of Mo_{diss} during the reduction of Mn oxides in the surface sediments when anoxic conditions reach the uppermost sediment layer (Burdige and Nealson, 1985). However, the water column data from both sites did not clearly support a direct relation between Mo_{diss} and Mn_{diss} dynamics within the study area (Figs. 2a and 3a). Although a certain relation might be inferred from slightly increasing Mo_{diss} values in spring at Spiekeroog Site, distinctly lower Mn_{diss} enrichments at Sylt Site argue against a significant release of Mo due to the reduction of Mn oxides in the surface sediments. This is also true for reduction of Fe-oxihydroxides as seen in pore water profiles from Spiekeroog Site showing no relation between Fe and Mo dynamics (Kowalski et al., 2009). Assuming a comparable Mo content of the sedimentary Mn oxides at both sites, the about four-times higher Mn maxima at Spiekeroog, e.g. in spring 2008 and 2009, should lead to much more pronounced positive concentration anomalies.

High concentrations after depletion periods at the Spiekeroog Site may be due to Mo_{diss} release from the sediments into the overlying water column after the occurrence of high Mo_{diss} enrichments in the pore waters (Dellwig et al. 2007; Kowalski et al., 2009). Furthermore, sediment resuspension due to wind-induced wave action and tidal currents during tidal drainage and inundation (Roman and Tenore, 1978; Lavelle et al., 1984; de Jonge and van Beusekom, 1995; Christiansen et al., 2004, 2006; Sterckx et al., 2007; Bartholomä et al., 2009) may contribute to Mo inventories. Intense sediment displacement and transport

influencing biogeochemical element budgets have been reported especially during storm events (e.g. You, 2005; Grunwald et al., 2009; Bartholomä et al., 2009; Kolditz et al., 2012). Busch et al. (1998) observed a clear seasonality of strong wind and storm events occurring mainly in autumn and winter months. As shown in Figure 6a, even wind speeds of about 12 m s⁻¹ (6 bft) were able to increase SPM concentrations significantly. As the permanently oxidised sediment layer is only a couple of millimetres thick during the summer months (Jansen et al., 2009) and local areas with reduced sediment surfaces, so called “black spots”, may occur (Böttcher et al., 1998; Böttcher 2003), resuspension may transfer reduced sediment components as iron-monosulphides (FeS) and associated trace elements like Mo into the oxic water column (Fig. 6b).

An oxidation experiment with natural anoxic sand and mixed flat sediments was carried out to estimate the amount and rate of Mo potentially released during sediment resuspension. The results showed a rapid Mo_{diss} release from the sediments within the first hour reaching maximum values of 0.75 µM for the sand and 4 µM for the mixed flat sediment (Fig. 7a). Further differences between the sediment types were visible in the rates of Mo_{diss} release (Fig. 7b). In the initial phase of the experiment (>15 min) around 0.1 g m⁻³ h⁻¹ more Mo was released from the sand than from the mixed flat sediment. The decrease in oxidation rate and the different steady-state levels were due to differences in the Mo pool sizes and the initial reactive particle surfaces. The isotopic composition of the released Mo_{diss} (Fig. 7c) matched the sedimentary isotope data (Table 1). Although Mo isotope data for Mo_{diss} in the water column during positive Mo concentration anomalies are not available, these results suggest an intense release of isotopically light Mo from the sediments to the water column possibly also causing a shift to a lighter isotopic composition of the water column. Table 1 compares the Mo contents and isotopic composition of sandy surface sediments (from site JS) with typical oxidised surfaces with those which were reduced and coloured black by iron sulphides. The latter should be in particular sensitive to modifications upon storm- or current-induced resuspension. Compared to the oxidised surfaces they are slightly higher enriched in the contents of total Mo and the heavy stable Mo isotope, likely due to a slightly higher fixation of Mo from pore waters under sulphidic conditions.

Figure 8 shows results of a model simulation estimating residence times of mud particles (diameter 50 µm) in the water column over a tidal cycle during calm conditions (Fig. 8a) and the storm event “Britta” from 31 October to 2 November 2006 (Fig. 8b) as well as the difference between both situations (Fig. 8c). During calm conditions, highest residence times due to elevated current velocities were generally seen in the main tidal channel reaching more

than 10 hours (Fig. 8a). At the tidal flat margins particles were still suspended around 5-7 hours while on the tidal flats suspension was shortest (<2 hrs) due to a lower water level (<2m) and less tidal activity.

During the storm event, high erosion and particle resuspension occurred at the northern coasts of the barrier islands due to elevated wave energy (Fig. 8b). On the sand flats within the backbarrier area resuspension was also enhanced (2-4 hrs, Fig. 8c) as the winds from north-westerly direction (Bartholomä et al., 2009) pushed the water masses into the backbarrier area against the ebb current thereby extending duration of water coverage on the tidal flats.

Essential sediment erosion down to 16 cm sediment depth was observed during a storm event in the backbarrier area of Spiekeroog Island by Tilch (2003). This area is even subjected to pronounced sediment displacement under normal conditions as indicated by own observations revealing maximum erosion of about 8 cm in April 2008 and still about 5 cm in summer during wind speeds reaching only up to 16 m s^{-1} (data not shown).

Based on the experimental Mo release rates and the particle tracking model a rough calculation was made to elucidate the potential impact of resuspension on the Mo budget in the open water column. To assure conformity with sediment-water ratio in the study area, which was approximated to 0.08 (74 km² area, Walther, 1972; $145 \times 10^6 \text{ m}^3$ water volume, Lübben et al., 2009; assumed sediment depth of 1 cm = $1.1 \times 10^9 \text{ kg}$ sediment and $145 \times 10^9 \text{ L}$ seawater) the experimental results (Fig. 8a; sediment-water ratio = 2) were adjusted with a factor 0.04 (sediment-water ratio study area / sediment-water ratio experimental setup). When considering a homogenous sediment erosion of 5 cm depth (1 cm oxic zone + 4 cm anoxic sediment) and a sediment distribution of 62% sand flat and 38% mixed/mud flat in the back barrier area of Spiekeroog Island (Al-Raei et al., 2009), $2.8 \times 10^9 \text{ kg}$ anoxic sand and $1.4 \times 10^9 \text{ kg}$ anoxic mixed/mud flat sediments may be suspended in the water column. Assuming a mean residence time of the sediment particles within the oxic water column of two hours, the Mo_{diss} level may be increased by about 25 nM. Thus, in addition to Mo release from deposited organic-rich particles, resuspension is able to considerably affect the pelagic Mo budget and most likely represents an important mechanism contributing Mo to the open water column.

5. Conclusions and outlook

Temporary Mo depletions of 50% of the usual level were found repeatedly in the water column of the German Wadden Sea in early summer between 2007 and 2011, thus representing a typical feature of this ecosystem. The major processes influencing the Mo

cycle in the investigated coastal system are summarized in Fig. 9. As Mo depletions often appeared during/after breakdown of algae blooms, a coupling to algae-derived organic matter is feasible. Especially during the summer months, *Phaeocystis*-derived organic mucus is probably able to trap significant amounts of dissolved Mo which is subsequently transferred to the surface sediment after aggregation of particles and organic matter. Associated Mo isotope fractionation of dissolved Mo during a negative Mo concentration anomaly is assumed to be caused by bonding of Mo to algae-derived organic matter. During the decomposition of deposited organic matter, Mo may be released again leading to significant Mo enrichments in the shallow pore waters.

Besides Mo removal from the water column, Mo concentrations exceeding the salinity-based theoretical values were observed. Laboratory experiments and modelling approaches suggest a significant contribution of resuspended anoxic surface sediments during tidal wave action and storm events on water column Mo budgets due to oxidative release of sulphide-bound Mo. The transfer of isotopically light molybdate, released from degraded organic material or from reoxidised sulphidic sediments, into the water column probably closes the isotope balance between burial of isotopically light Mo adsorbed to aggregates and recycling of light Mo into the water column. The present study shows for the first time the importance of benthic-pelagic coupling for the Mo mass balance in a tidal system based on stable Mo isotope fractionation.

Future work may also focus on the relevance of Mo removal from oxic surface waters and associated Mo isotope fractionation during periods of high productivity in ancient near-coastal systems e.g. during Proterozoic and Mesozoic oceanic anoxic events (OAE) as isotopic pre-fractionation of Mo in oxic surface waters may influence the sedimentary signatures (e. g. Helz et al., 1996; Arnold et al., 2004; Wille et al., 2007). Additionally to the impact of sulphide concentrations (Neubert et al., 2008) as well as metal oxide cycles on the Mo isotopic composition (Reitz et al., 2007), a transfer of isotopically light Mo to the underlying anoxic/sulphidic water body or sediment of a stratified coastal system via sinking aggregates may be assumed.

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Table 1: Mo concentrations/contents and isotopic composition in the water column, SPM, and sediments at Spiekeroog Site and of biota collected from different sites. Uncertainties of $\delta^{98/95}$ Mo represent run precisions. External reproducibility is +/- 0.06 (2s).

Sample	$\delta^{98/95}\text{Mo}$	2σ	Mo [nM]
Water column			
29 Apr 2008	2.23	0.05	110
16 June 2008	2.52	0.04	60
24 June 2008	2.45	0.05	50
11 Aug 2008	2.37	0.05	90
23 Sept 2008	2.25	0.06	100
28 June 2007	-	-	70
19 July 2007	-	-	130
4 Sept 2007	-	-	90
SPM			
28 June 2007	0.28	0.03	0.60
19 July 2007	0.93	0.06	0.31
4 Sept 2007	1.09	0.05	1.07
Sediment			mg kg⁻¹
<i>Janssand July 2006:</i>			
Oxic surface: 0.8-1.0 cmbsf	0.34		0.10
8.0-10.5 cmbsf	0.56		0.12
Anoxic surface: 0-1.0 cmbsf	0.79		0.16
9.0-10.5 cmbsf	0.89		0.12
<i>27 Mar 2008: (used for experiments)</i>			
Anoxic sandy sediment (JS)	0.46	0.06	0.44
Anoxic mixed sediment (NN)	1.45	0.03	1.31
Periostraca			mg kg⁻¹
<i>Mytilus edulis</i>	-	-	8

Ensis americanus

Sylt June 2009	-	-	118
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Ensis americanus

Sylt Nov 2009	-	-	256
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Ensis americanus

Norderney Jan 2010	1.29		160
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Figure captions

Fig. 1: Map of the study areas in the German Wadden Sea;

A) Backbarrier area of Spiekeroog Island with sampling sites for seawater (OB, time series station) and sediments (Janssand, JS, Neuharlingersieler Nacken, NN).

B) Sylt-Rømø tidal basin (Sylt Island) with sampling site LL.

Fig. 2: Time series of a) dissolved molybdenum (open circles: measured values; black circles: calculated from salinity, black arrows indicate the most prominent positive concentration anomalies) and manganese (grey circles), b) water temperature and cell carbon of diatoms (open squares) and *Phaeocystis sp.* (black squares) in the water column of the backbarrier area of Spiekeroog Island. The grey line marks the usual seawater value of Mo.

Fig. 3: Time series of a) dissolved molybdenum (open circles: measured values; black circles: calculated from salinity, black arrows mark the most prominent positive concentration anomalies) and manganese (grey circles), b) water temperature and cell carbon of diatoms (open squares) and *Phaeocystis sp.* (black squares) in the water column of the Sylt-Rømø tidal basin. The black arrow indicates a further increase of cell carbon in March 2010 up to 1202 $\mu\text{g L}^{-1}$. The grey line marks the usual seawater value of Mo.

Fig. 4: a) Mo_{diss} concentrations (black circles) in the water column of Site Spiekeroog (OB) during the depletion period in 2008 with corresponding $\delta^{98/95}\text{Mo}$ values (open circles). The grey line marks the mean ocean molybdenum value (MOMo). Error bars indicate measurement uncertainties. b) Scatterplot of Mo_{diss} and $\delta^{98/95}\text{Mo}$ showing a distinct negative correlation of $r = -0.94$. The grey circle denotes the MOMo.

Fig. 5: Estimation of Mo isotope fractionation with a calculated enrichment factor using a Rayleigh-based equation and comparison with factors determined during Mo scavenging by Mn oxides (*Wasylenki et al., 2008) and FeOOH (**Goldberg et al., 2009) and by biological Mo uptake (**Zerkle et al., 2011).

Fig. 6: a) Wind speed (*open circles*) and SPM concentrations (*black circles*) in the backbarrier area of Spiekeroog Island in August 2003.

b) Anoxic surface sediments are suspended in the main tidal channel at the eastern margin of the Jansand flat after a change from an eastern to a north-western wind regime (spring 2006; photo: M.E. Böttcher). The black colour (*arrows*) is caused by resuspension of iron monosulphide-rich sediment material.

Fig. 7: Oxidation experiment with natural anoxic sand flat (*grey open circles*) and mixed flat (*black circles*) sediments suspended in oxygenated artificial seawater; a) concentration of dissolved Mo versus the time of the experiment; b) calculated rates of Mo release from the sediments during oxidation; c) Isotopic composition of the released Mo_{diss} .

Fig. 8: Model-derived residence times of suspended particles (grain size diameter 50 μm) in the water column of the backbarrier area of Spiekeroog Island a) during calm weather conditions, and b) during the storm event “Britta” (November 2006). Figure c) presents a difference map (b minus a).

Fig. 9: Generalised illustration of the benthic-pelagic interactions influencing the Mo cycle in a tidal system.

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b)

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