

Trace metal dynamics in the water column and pore waters in a temperate tidal system: response to the fate of algae-derived organic matter

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Abstract Tidal and seasonal behaviour of the redox-sensitive trace metals Mn, Fe, Mo, U, and V have been investigated in the open-water column and shallow pore waters of the backbarrier tidal flats of the island of Spiekeroog (Southern North Sea) in 2002 and 2007. The purpose was to study the response of trace metal cycles on algae blooms, which are assumed to cause significant changes in the redox state of the entire ecosystem. Trace metal data were complemented by measurements of nutrients and enumeration of algae cells in 2007. Generally, Mn and V show a tidal cyclicity in the water column with maximum values during low tide which is most pronounced in summer due to elevated microbial activity in the sediments. Mo and U behave almost conservatively

throughout the year with slightly increasing levels towards high tide. Exceptions are observed for both metals after summer algae blooms. Thus, the seasonal behaviour of the trace metals appear to be significantly influenced by productivity in the water column as the occurrence of algae blooms is associated with an intense release of organic matter (e.g. transparent exopolymer particles, TEP) thereby forming larger organic-rich aggregates. Along with elevated temperatures in summer, the deposition of such aggregates favours microbial activity within the surface sediments and release of DOC, nutrients and trace metals (Mn, Mo and V) during the degradation of the aggregates. Additionally, pronounced reducing conditions lead to the reduction of Mn(IV)-oxides and Fe(III)-(oxi)hydr)oxides, thereby releasing formerly scavenged compounds as V and phosphate. Therefore, pore-water profiles show significant enrichments in trace metals especially from July to September. Finally, the trace metals are released to the open water column via draining pore waters (esp. Mo, Mn, and V) and/or fixed in the sediment as sulphides (Fe, Mo) and bound to organic matter (U). Non-conservative behaviour of Mo in oxygenated seawater, first observed in the investigation area by Dellwig et al. (*Geochim Cosmochim Acta* 71:2745–2761, 2007a), was shown to be a recurrent phenomenon which is closely coupled to bacterial activity after the breakdown of algae blooms. In addition to the postulated fixation of Mo in oxygen-depleted micro-zones of the aggregates or by freshly formed organic matter, a direct removal of Mo from the water column by reduced sediment surfaces may also play an important role.

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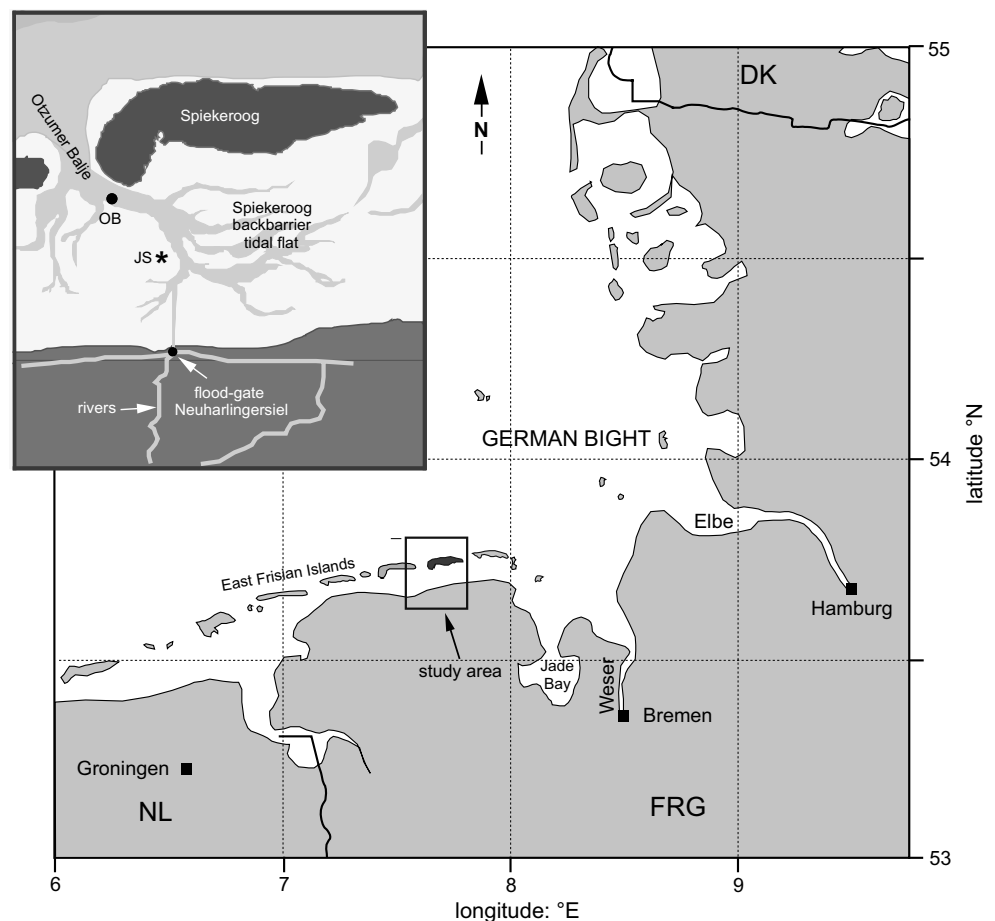
1 Introduction

The backbarrier tidal flats of the East Frisian island chain form the transition zone between the terrestrial and marine realm (Fig. 1). Such ecosystems are subject to pronounced dynamics caused by distinct tidal and seasonal changes of physical, chemical and biological parameters significantly influencing biogeochemical element cycles (e.g. de Jonge et al. 1993; Raabe et al. 1997; van Beusekom et al. 1999; Philippart et al. 2000; van Beusekom and De Jonge 2002; De Beer et al. 2005; Lunau et al. 2006; Dellwig et al. 2007a, b). Especially redox-sensitive trace metals like Mn or Mo are promising candidates for reflecting variations in bioproductivity and microbial activity. Dellwig et al. (2007b), for instance, investigated the tidal and seasonal behaviour of Mn in the water column of the study area and reported a strong relationship between water column signatures and microbial activity within the underlying sediments. Additionally, Bosselmann et al. (2003), Dellwig et al. (2007a, b), and Beck et al. (2008a) found pronounced dynamics of redox-sensitive trace metals in the top sediments which appear to be controlled by redox stratification and deposition of detrital inorganic matter.

As a consequence of the different electro-chemistry of redox-sensitive trace metals their response to changing redox conditions varies. While U, Mo and V occur as soluble oxyanions in oxygenated seawater, Mn is only soluble under reducing conditions (e.g. Morris 1975; Collier 1985; Burdige 1993; Shiller 1997; Statham et al. 1998; von Langen et al. 1997). The trace metals can be stabilised in the dissolved phase by complexation with inorganic (carbonate, chloride, phosphate and sulphate) or organic ligands (fulvic, humic acids). They further can be removed from the water column by “scavenging” on organic (Hoffman and Fletcher 1981) or inorganic particles (Goldberg 1954; Balistrieri et al. 1981), assimilation by organisms (Cole et al. 1993) or co-precipitation with minerals (e.g. sulphides, Huerta-Diaz and Morse 1992). Hence, the response of trace metals in the open water column and the pore waters to changing redox conditions should provide information about the state of the investigated ecosystem.

The major aim of this contribution is to draw attention to the response of selected redox-sensitive trace metals (Mn, Mo, U, V, Fe) to changes in bioproductivity,. Therefore, tidal and seasonal characteristics of trace metals in the open-water column and in the pore waters of surface

Fig. 1 Map of the study area showing the backbarrier tidal flats of Spiekeroog Island, Wadden Sea (NW Germany). The detailed map presents sampling sites in the tidal inlet (Otzumer Balje, *OB*) and on the Janssand tidal flat (*JS*)



sediments were investigated during several sampling campaigns in the backbarrier tidal flats of the island of Spiekeroog (NW Germany). In 2007, trace metal dynamics are accomplished by measurements of nutrients, sulphur species and algae cell numbers.

2 Geochemistry of selected redox-sensitive trace metals

In oxic sea water, *uranium* (U) behaves conservatively as soluble U(IV) carbonate complex but can be reduced enzymatically by microorganisms (Lovley et al. 1991, 1993) leading to insoluble U(IV) (uranyl). Additionally, U shows a strong tendency towards complexation with organic matter (Klinkhammer and Palmer 1991).

Molybdenum (Mo) occurs as soluble molybdate anion (MoO_4^{2-}) in oxygenated seawater and is generally assumed to behave conservatively, i.e. it follows salinity (Bruland 1983; Collier 1985). However, some deviations from conservative behaviour have been reported by several authors for various ecosystems. For instance, Head and Burton (1970) and Cole et al. (1993) observed Mo removal from oxic estuarine waters which was explained by plankton assimilation and adsorption on organic matter. Yamazaki and Gohda (1990) also suggested that organic Mo capture by biological activity could be responsible for Mo depletion in shallow coastal and oceanic waters. Such association of Mo with particulate organic matter was earlier mentioned by Szilagy (1967) and Nissenbaum and Swaine (1975). As a further process of Mo removal from the water column, Berrang and Grill (1974) explained decreasing Mo values in the water column of Saanich Inlet by Mo scavenging via freshly formed MnO_x phases. More recently, Tuit and Ravizza (2003) observed both Mo enrichment and depletion in the equatorial Pacific. The authors suggested a strong relationship between Mo and cyanobacteria growth. Dellwig et al. (2007a) reported extreme Mo depletion in coastal waters of the Southern North Sea and postulated Mo fixation in oxygen-depleted micro-zones of large aggregates and/or scavenging by freshly formed organic matter. In sulphidic waters, however, MoO_4^{2-} is sequentially transformed to particle-reactive thiomolybdates (Erickson and Helz 2000) which are predominantly captured by iron sulphides (Helz et al. 2004; Vorlicek and Helz 2002; Vorlicek et al. 2004) or particulate organic matter. Thus, molybdenum removal by anoxic or even euxinic sediments by sulphide–organic matter–Mo interactions presumably forms the ultimate process for Mo burial (Helz et al. 1996; McManus et al. 2002, 2006; Algeo 2006; Neubert et al. 2008).

Variations of *vanadium* (V) are also linked to salinity but with a slight salinity-independent surface depletion in ocean waters. V occurs in three oxidation states: As V(V) forming

soluble oxyanions, e.g. H_2VO_4^- and HVO_4^{2-} , and under reducing conditions as V(IV), forming the oxocation VO (II) (vanadyl), and V(III). Reduction of V(V) is assumed to be caused by sulphide (Wehrli and Stumm 1989; Wanty and Goldhaber 1992) leading to particle-reactive species which precipitate as oxyhydroxides (Wehrli and Stumm 1989) or form stable complexes with humic acids (Szalay and Szilagy (1967).

Reactive *iron* (Fe) occurs under oxic conditions as Fe (III)-(oxyhydr)oxides and can be reduced chemically by sulphide (Poulton 2003) or enzymatically by Fe(III)- and sulphate-reducing bacteria to Fe^{2+} (Lovley et al. 1993). Depending on the availability of reactive iron the reduction of Fe(III) in a sulphide-containing system results in the formation of Fe-sulphide minerals like Fe-monosulphides and pyrite (e.g. Berner 1984; Canfield 1989; Canfield et al. 1992).

Due to the slow oxidation rate, dissolved *manganese* (Mn^{2+}) is relatively stable in oxic waters, e.g. as chloro-complexes (Roitz et al. 2002). Bacterially catalysed or photochemical Mn^{2+} oxidation leads to precipitation of Mn oxides (Emerson et al. 1982; Anbar and Holland 1992; Nico et al. 2002) which have the ability to trap other trace metals by “scavenging” (e.g. Feely et al. 1983; Koschinsky et al. 2003). Suboxic and anoxic conditions favour microbial reduction of Mn(IV) (Burdige and Neelson 1985) thereby releasing scavenged trace metals. Recently, Trouwborst et al. (2006) reported the occurrence of Mn^{3+} in the suboxic zone of the Black Sea water column as an important intermediate during bacterial oxidation of Mn^{2+} .

3 Geographical setting

The Wadden Sea system of the Southern North Sea extends over a length of 450 km from Den Helder (Netherlands) in the West to Esbjerg (Denmark) in the North. The development of the coastal area started about 7,500 BP with the Holocene sea-level rise. The mesotidal regime of the East Frisian Wadden Sea (tidal amplitude, 2.2 to 2.8 m) formed a complex system of barrier islands and backbarrier tidal flats (Streif 1990). Deep inlet channels between the islands enable water and material exchange with the open North Sea.

Sampling sites of this work are located in the backbarrier tidal flat of the island of Spiekeroog which is situated in the East Frisian Wadden Sea of NW Germany (Fig. 1). Surface water samples were taken in the tidal inlet between the islands of Spiekeroog and Langeoog (Otzumer Balje, OB) near a time series station located at position $53^\circ 45' 01.00'' \text{N}$, $7^\circ 40' 16.30'' \text{E}$ (Grunwald et al. 2007). Sampling of pore waters and sediments was carried out on the Janssand (JS), a sand flat (position $53^\circ 43' 57.72'' \text{N}$, $7^\circ 41' 17.00'' \text{E}$) which

becomes exposed during low tide (Fig. 1). The high permeability of sandy sediments enables advective pore water transport which leads to more effective organic matter degradation and nutrient release whereas processes in muddy sediments often are more influenced by diffusion (Billerbeck et al. 2006; Franke et al. 2006).

4 Materials and methods

4.1 Sampling

In 2002, surface water samples for the analysis of dissolved and particulate matter were taken during four cruises aboard R/V “Senckenberg” at position OB (Fig. 1). Depending on suspended particulate matter (SPM) concentrations, 0.15 to 1.25 L of water were filtered through pre-weighed Millipore Isopore® membrane filters (0.45 µm polycarbonate (PC), for multi-element analyses) and Whatman glass microfibre filters GF/F (0.7 µm glass fibre [GF], for TC and TIC analyses). Filters were rinsed with purified water, dried at 60°C for 48 h and re-weighed for the determination of total SPM. Samples for the analysis of dissolved metals were directly taken with pre-cleaned PE-syringes and 0.45 µm SFCA syringe filters. These samples were acidified with HNO₃ (supra pure, Merck) to 1% (v/v) and stored in pre-cleaned PE bottles. Tidal creek water samples (five samples for each cruise) were also directly taken with syringes. Pore waters were sampled with portable lances. The samples were subsequently treated in the same way as the seawater samples.

In 2007, sampling of seawater and suspended particulate matter (SPM) from the upper 1 m of the water column was performed with a multi water sampler (Hydro-Bios, Kiel, Germany) aboard of R/V “Navicula” (Carl von Ossietzky University, Oldenburg). Pore water was sampled with an in situ pore-water sampler which is permanently installed in the tidal-flat sediments and reaches a maximum depth of 5 m (Beck et al. 2007). This communication only focuses on pore water from the uppermost metre. For data from deeper parts of the sediment column, the authors refer to Beck et al. (2008a, b).

Seawater and pore-water samples were rinsed through 0.45 µm SFCA syringe filters. Samples for metal analyses were acidified to 1% (v/v) with HNO₃ (supra pure, Merck). For determination of hydrogen sulphide (H₂S), 2 ml of filtered sample were fixed in a PE vial with 100 µl of 5% zinc acetate solution.

For SPM determination during the campaigns in 2007, 0.5 to 1.5 L seawater was filtered through pre-weighed PC filters (Millipore Isopore membrane filters, 0.4 µm pore size). After rinsing the filters with approx. 100 ml purified water they were dried at 60°C for 48 h.

4.2 Geochemical analysis

For analysis of particulate metals the PC filters were completely digested with an acid mixture of HNO₃, HClO₄ and HF in a PDS-6 pressure digestion system (Loftfields Analytical Solutions) at 180 °C for 6 h and measured by ICP-OES (Thermo, iCAP 6300 Duo). A more detailed description of these procedures is given by Dellwig et al. (2007a, b). Water samples were measured using ICP-OES (Thermo, iCAP 6300 Duo) and HR-ICP-MS (Thermo Finnigan, Element 1 and 2). For ICP-MS measurements the samples were diluted 25-fold according to the method published by Rodushkin and Ruth (1997) and twofold for ICP-OES.

Sulphide was determined after the method described by Cline (1969). A diamine reagent (*N,N*-dimethyl-*p*-phenylenediamine sulphate and ferric chloride diluted in hydrochloric acid) was added to a sample aliquot. After a reaction time of 20 min, the absorbance was measured photometrically (Analytik Jena AG, Specord 40) at a wavelength of 670 nm. Sulphate was also determined by photometry (wavelength 450 nm) after the method described by Tabatabai (1974) using aliquots from ZnAc-fixed samples after centrifugation.

DOC was measured by temperature catalytic oxidation (Analytik Jena AG, multi N/C 3000 analyser) using K-hydrogenphthalate for external calibration.

Photometric measurements of the nutrients phosphate, ammonium and silica in pore waters were performed using the methods described by Grasshoff et al. (1999). Determination of total alkalinity followed the method described by Sarazin et al. (1999). Silica in surface water was determined by automated nutrient analysers installed at the time series station and based on a loop-flow reactor and loop-flow analysis technique. A detailed description of the time series station and the nutrient analyzer setup can be found in Grunwald et al. (2007).

4.3 Phytoplankton count

For phytoplankton cell count, seawater samples (2.5 L) were filtered through plankton nets with 10 µm mesh size. The cells were preserved by the addition of Lugol solution and stored in PE bottles at 4°C. Phytoplankton cells were enumerated according to the method by Utermöhl (1958). Aliquots of the concentrated samples were stored overnight in 10-ml chambers to enable sedimentation of the cells. Analyses were performed with an inversion microscope (Zeiss Axiovert 100), and the cells were counted in two or three diametrical transects across the whole chamber. Two-hundred-fold magnification was used to identify species with high abundances and small cell size; afterwards, 100-fold magnification was used for species with small abundance and large cell size.

5 Results and discussion

5.1 Influence of algae blooms on tidal-flat sediments

The Wadden Sea is subject to drastic short-term changes due to the general influence of the tidal regime and changes in primary production, mainly by microalgae. The occurrence of algal blooms during spring and summer leads to an intense consumption of nutrients and subsequently a high production of biomass in the water column. Figure 2 shows phytoplankton cell counts and the corresponding variations in silica from April until the end of August 2007. Cell numbers of diatoms increase distinctly during mid-April reflecting the onset of the spring bloom. The time offset of about 2 weeks which is obvious between decreasing silica concentrations and increasing diatom cells in April has methodological reasons as only diatoms larger than 10 μm were sampled. Therefore, the apparent beginning of the bloom is delayed due to the exclusion of smaller cell sizes in the present sampling protocol (Heike Simon, personal communication). On the basis of these diatom counts, the bloom lasted for about 2 weeks and was paralleled by elevated numbers of *Phaeocystis* species. During breakdown of the spring bloom, which is caused by the reduced availability of nutrients in the open-water column, the values of silica increased again and showed some fluctuations afterwards. In early June, a second diatom bloom occurred which lasted for about 10 days in the study area. A significant increase in silica values marks the breakdown of this second bloom in mid-June. In the following time-period, only slight changes in diatom numbers and some variations in silica occurred.

An important consequence of algae lysis is the pronounced release of DOC (Dellwig et al. 2007a) and nutrients (Martens and Elbrächter 1997) to the water column. Thus, high amounts of organic compounds like TEP (transparent exopolymer particles) are released. In contrast to the spring bloom when microbial activity is comparatively low, the microbial biomass decomposition is

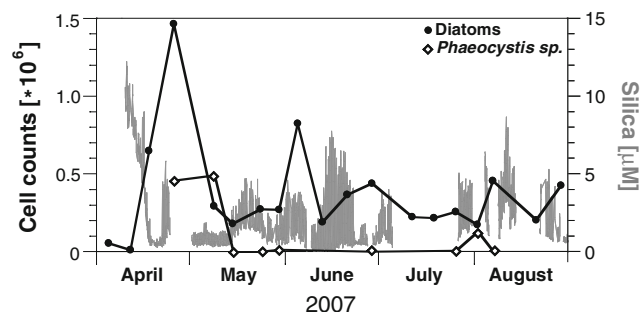


Fig. 2 Silica concentrations and diatom cell counts in the water column of the Spiekeroog Island backbarrier area in 2007

much more intense during the summer months (Dellwig et al. 2007a) resulting in the production of sticky carbohydrates which colligate suspended inorganic and organic particles in the water column thereby forming larger aggregates (Passow 2002; Chen et al. 2005). The resulting aggregates hydraulically behave differently and sinking velocities resemble of coarser-grained material. Therefore, significant amounts of aggregates are deposited on the tidal-flat sediments forming a fluffy layer of organic-rich material on the sediment surface (Chang et al. 2006). Subsequently, the deposited organic-rich aggregates are incorporated into the upper first centimetres of the sediment by tidal forces (Rusch and Huettel 2000; Billerbeck et al. 2006). These coupled processes result in a supply of freshly formed and readily degradable marine organic matter to the sediments. Along with increasing temperature in summer, the organic matter input leads to elevated activity of microorganisms in the upper sediment layer (Böttcher et al. 1999, Bosselmann et al. 2003).

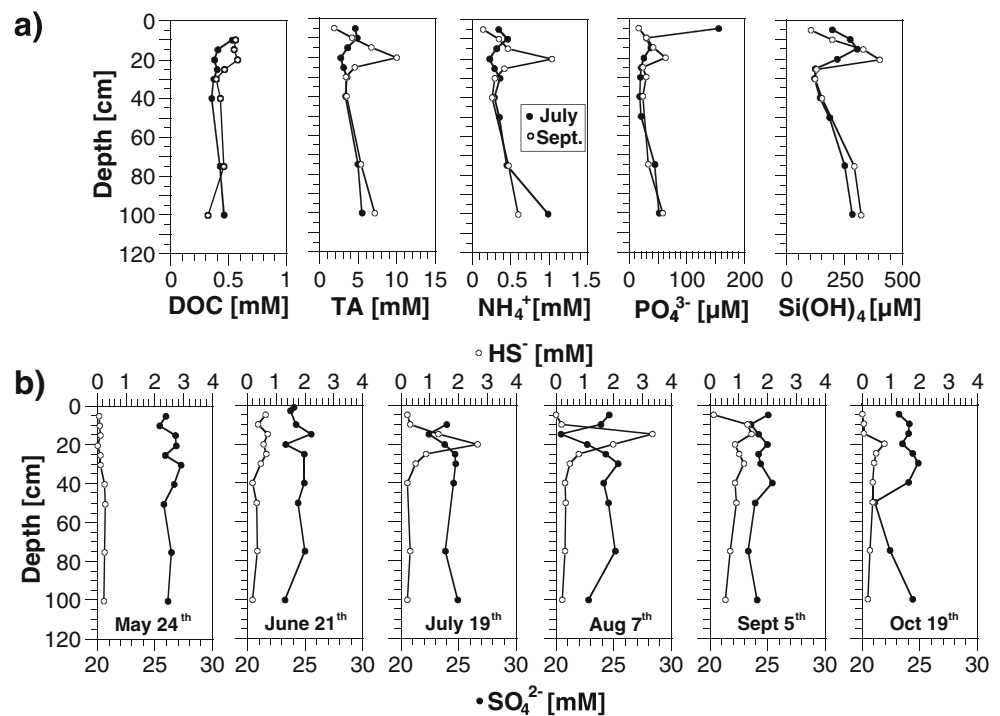
In the pore-water profiles, DOC, total alkalinity (TA), ammonium and phosphate (Fig. 3a), which represent products of organic matter degradation, are clearly enriched as seen in the depth interval of around 20 cm after the summer bloom when comparing data from July and September 2007. Along with the increase in HS^- and parallel decreasing SO_4^{2-} values in July and August 2007 (Fig. 3b), these enrichments can be explained by elevated microbial activity, which is favoured by the organic matter input after the algae bloom breakdown in June.

In contrast, elevated phosphate values in September are most likely caused by dissolution of Fe(III)-(oxyhydr)oxides due to pronounced reducing conditions in the sediments during late summer. Iron phases are known to adsorb PO_4^{3-} during formation, which are again released when solid phases are reduced (e.g. van Raaphorst and Kloosterhuis 1994).

The variations of silica in the pore waters are less pronounced as dissolution of diatom frustules is a relatively slow process which seems to occur throughout the entire year, resulting in an almost-constant release of silica out of the sediment (Beck et al. 2008b). Thus, increasing concentrations of silica after collapsing algae blooms (Fig. 2) are more likely the result of advective pore-water release (Billerbeck et al. 2006; Beck et al. 2008a, b) and reduced consumption rather than decomposition of diatoms within the water column. While the lysis of algae cells is a comparatively fast process, their frustules are stable for longer time periods, are therefore deposited on the sediment surface and enter slightly deeper layers due to tidal forces (e.g. Rusch and Huettel 2000).

Overall, algae- and temperature-induced increases in microbial activity in the water column and especially in the top sediment layers lead to a shift of redox conditions in the

Fig. 3 Concentrations of **a** DOC, TA, ammonium, phosphate and silica, and **b** hydrogen sulphide and sulphate in the pore waters at site JS in 2007



sediment and reduces the thickness of the oxic sediment surface layer. An example of such extreme changes in sedimentary redox conditions is the formation of anoxic sediment surfaces where sulphidic pore waters are drained out of the sediment (e.g. Böttcher et al. 1998, 1999; Böttcher 2003). Upward advective pore-water flow has been shown to be promoted by near-surface methane formation.

The data presented so far reveal intense interactions between water column and sedimentary processes. Thus, seasonal variations in the top sediments are remarkably influenced by bioproductivity in the open-water column. The following chapters provide an insight into the interaction of both reservoirs with respect to selected redox-sensitive trace metals.

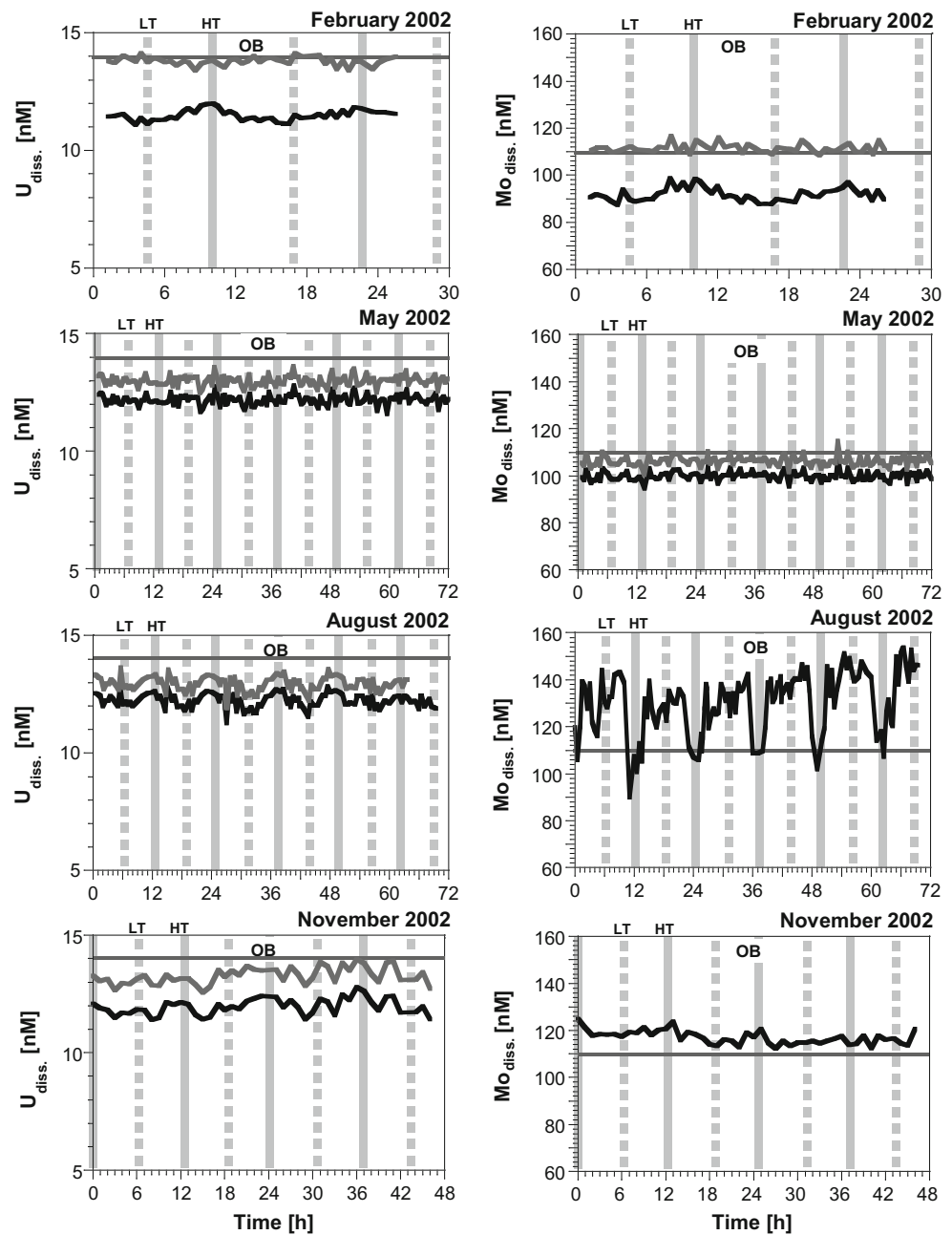
5.2 Uranium

The data from the Wadden Sea cruises in 2002 (site OB) show a general depletion of dissolved U (Fig. 4) when compared with the level in ocean waters (14 nM; Ku et al. 1977; Maeda and Windom 1982). In a first approximation, this difference is caused by the lower salinity in the Wadden Sea as the freshwater from continental run-off contributes only minor amounts of U (Table 1). Dissolved U shows a tidal pattern with maximum concentrations during high tide for most of the cruises. A normalisation to North Sea salinity smoothes the tidal pattern in February 2002 and moves all data points close to the ocean value (Fig. 4). In contrast, during the cruises in May and August 2002, when

salinity was distinctly higher and almost constant over the entire tidal cycles (Table 1), the normalised U concentrations increase only slightly and the general pattern remains unaffected. This finding contradicts a strictly conservative behaviour. Hence, the tidal variation of U in summer must be caused by other processes. Moreover, the depletion of U in the water column especially during low tide must be linked to processes like fixation of U within anoxic parts of the tidal-flat sediments (Klinkhammer and Palmer 1991; Shaw et al. 1994). This assumption is in accordance with measurements in August 2002 of pore waters and tidal creek waters draining out of the sediment during low tide, which are depleted in U (Fig. 5).

In the time series of 2007, U normalised to salinity shows a slight seasonal variation in the water column with depletion phases in April/May and June (Fig. 6) which is probably due to the breakdown of algae blooms and U sorption on organic particles. In 2002, U enrichment on SPM was insignificant (Fig. 7) but is probably masked by the geogenic background of U ($3.0 \mu\text{g g}^{-1}$; Wedepohl 1971). In pore waters, uranium is generally depleted in comparison to the water column due to a fast fixation in the sediment caused by complexation with organic matter and microbial reduction (e.g. Klinkhammer and Palmer 1991; Lovley et al. 1991, 1993). While the pore water shows depletion at 5 cm depth, higher concentrations occur at 10 to 25 cm depth with values around 5–6 nM from April to June (Fig. 8a). This behaviour is in agreement with investigations carried out by Morford et al. (2007). In addition, these authors found typical enrichments in the

Fig. 4 Seasonal variations of dissolved U and Mo in the water column of the Spiekeroog Island backbarrier area in 2002. Data presented in grey are normalised to offshore salinity. The grey line denotes the North Atlantic value; the vertical grey lines mark high tide (HT) and the dashed line low tide (LT)



uppermost centimetres (0–5 cm), due to diffusion from the open-water column into the sediment. Such a pattern is not reflected here as the first sampling occurred at 5 cm depth.

In July, an enrichment of U with respect to deeper parts of the profile is seen at 5 to 10 cm sediment depth. This enrichment increases to a maximum value of almost 12 nM in August (Fig. 8a). This behaviour could be the result of release from organic matter during its degradation and mineralization. Additionally, U release from reduced Fe (III)-(oxyhydr)oxides could also be responsible for the U enrichment in the uppermost sediment layers. In August 2007, the U concentrations in the water column reach the

seawater value (Fig. 6) most likely due to U release from sediments.

In the depth interval from 15 to 20 cm, U is removed from the pore water by reduction. This depth coincides with the depth of highest iron (Fe^{2+}) concentrations. The conformity of uranium reduction depth with reduction depth of iron was also described by Cochran et al. (1986), Zheng et al. (2002) and Morford et al. (2005) confirming the investigation results of Lovley et al. (1991) who found that U(VI) reduction is coupled with Fe(III)-reducing bacteria. U which is released during Fe (III)-(oxyhydr)oxide reduction may be directly fixed in the sediment.

Table 1 Average values and range (in parentheses) of salinity, SPM, POC and dissolved and particulate trace metals in the Wadden Sea and in freshwater flowing into the backbarrier area via flood-gates in Neuharlingersiel in 2002

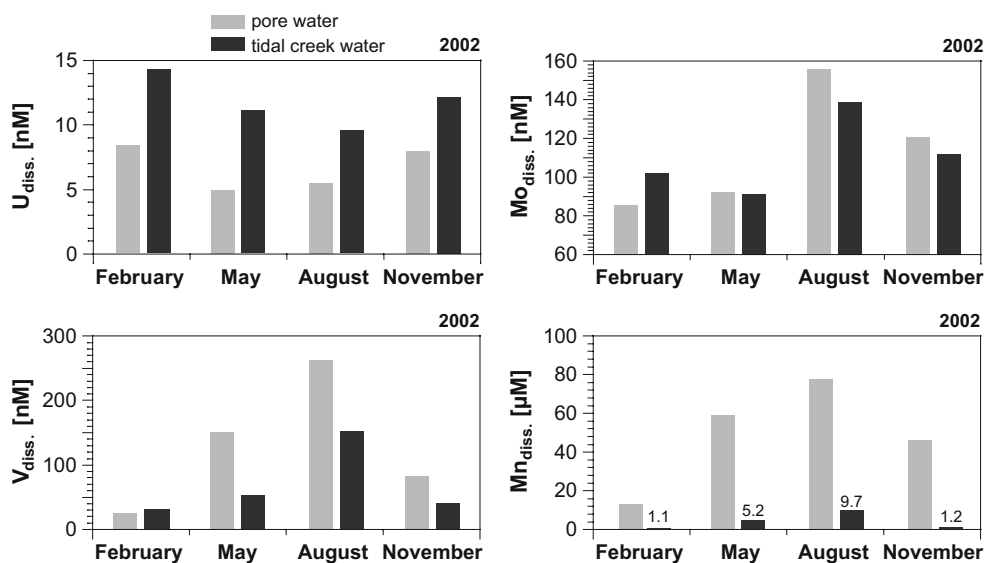
	Wadden Sea				Freshwater (flood-gate)	
	January	May	August	November	Winter	Summer
Salinity	27.2 (26.3-28.4)	30.9 (30.8-31.0)	31.2 (31.0-31.3)	29.5 (29.0-30.2)	1.7 (0.5-3.8)	2.1 (0.5-3.8)
DOC [mM]	0.24 (0.19-0.29)	0.21 (0.18-0.28)	0.21 (0.17-0.25)	0.21 (0.18-0.25)	1.3 (0.9-1.8)	1.2 (0.8-2.4)
Mndiss. [μM]	0.07 (0.02-0.16)	0.28 (0.07-0.58)	0.63 (0.14-1.1)	0.07 (0.01-0.16)	4.0 (2.2-6.3)	4.1 (0.8-8.4)
Modiss. [nM]	92 (86-100)	100 (95-105)	131 (94-155)	115 (110-121)	11 (6-19)	11 (4-19)
Fediss. [μM]	–	–	–	–	11 (6.5-19)	10 (0.1-31)
Udiss. [nM]	11.4 (10.8-12.0)	12.2 (11.6-12.8)	12.2 (11.3-12.9)	12.0 (11.4-14.5)	2.2 (0.9-4.2)	1.6 (0.7-4.0)
Vdiss. [nM]	36 (28-43)	34 (28-43)	53 (37-70)	32 (28-36)	45 (16-90)	86 (49-164)
SPM [mg l^{-1}]	62 (28-43)	12 (3.1-47)	8.4 (2.6-46)	45 (12-104)	24 (8.2-38)	37 (9.2-84)
POC [%]	3.6 (2.6-4.0)	5.2 (1.3-12)	4.3 (2.5-8.5)	4.2 (3.3-4.8)	8.6 (7.3-11)	13 (7.8-20)
Mnpart. [mg kg^{-1}]	763 (657-838)	1105 (626-3923)	1289 (676-1846)	903 (434-1046)	471 (333-687)	2,273 (698-5772)
Mopart. [mg kg^{-1}]	2.7 (1.6-7.4)	9.9 (1.1-8.3)	19 (4.6-83)	2.2 (1.6-4.7)	2.6 (1.6-4.3)	2.8 (0.9-9.5)
Fepart. [%]	3.6 (3.4-3.8)	2.9 (1.7-4.7)	2.8 (1.3-3.5)	3.7 (3.3-4.0)	8.3 (4.7-13)	7.0 (3.5-12)
$U_{\text{part.}}$ [mg kg^{-1}]	2.9 (2.5-3.3)	1.9 (1.3-3.0)	2.0 (0.9-3.1)	2.1 (1.7-2.4)	2.2 (1.8-2.6)	1.5 (0.9-2.1)
$V_{\text{part.}}$ [mg kg^{-1}]	133 (109-155)	100 (52-141)	98 (45-150)	125 (114-155)	153 (104-182)	136 (80-184)

5.3 Iron

In April 2007, dissolved iron shows elevated values of up to 88 μM in the pore water of the uppermost sediment layer (Fig. 8b), which is probably caused by intense reduction after the algae bloom in spring. Anoxic conditions may prevail during this period but with a presumably limited occurrence of sulphide (no sulphide measurements are available for April). Additionally, complexation with organic ligands favours solubility of Fe as shown by Luther et al. (1996). In the salt marshes of the island of Langeoog, Kolditz et al. (2009) observed Fe enrichments and complexation by organic compounds in an anoxic system without any significant net sulphate reduction.

With increasing temperature the onset of sulphide production is assumed to occur from May to July leading to Fe fixation in the sediment as FeS. Temperature has been shown to be one of the two major drivers for microbial sulphate reduction in the intertidal sands (Al-Raei et al. 2009). Although less pronounced, Fe^{2+} concentrations increase again in August and reach a maximum value of 28 μM . Along with organic-rich aggregates deposited in the surface sediment Fe(III)-(oxi)hydr)oxides are transferred to the sediment where they may be reduced by sulphide. The Fe(III) content of sinking aggregates is close to the geogenic background as seen in the enrichment factors (EF) of SPM of 1.1 (4.83 $\mu\text{g g}^{-1}$; Wedepohl 1971). However, leaching experiments carried out by Hinrichs et

Fig. 5 Seasonal variations of dissolved U, Mo, V and Mn in pore waters and tidal creek waters in 2002



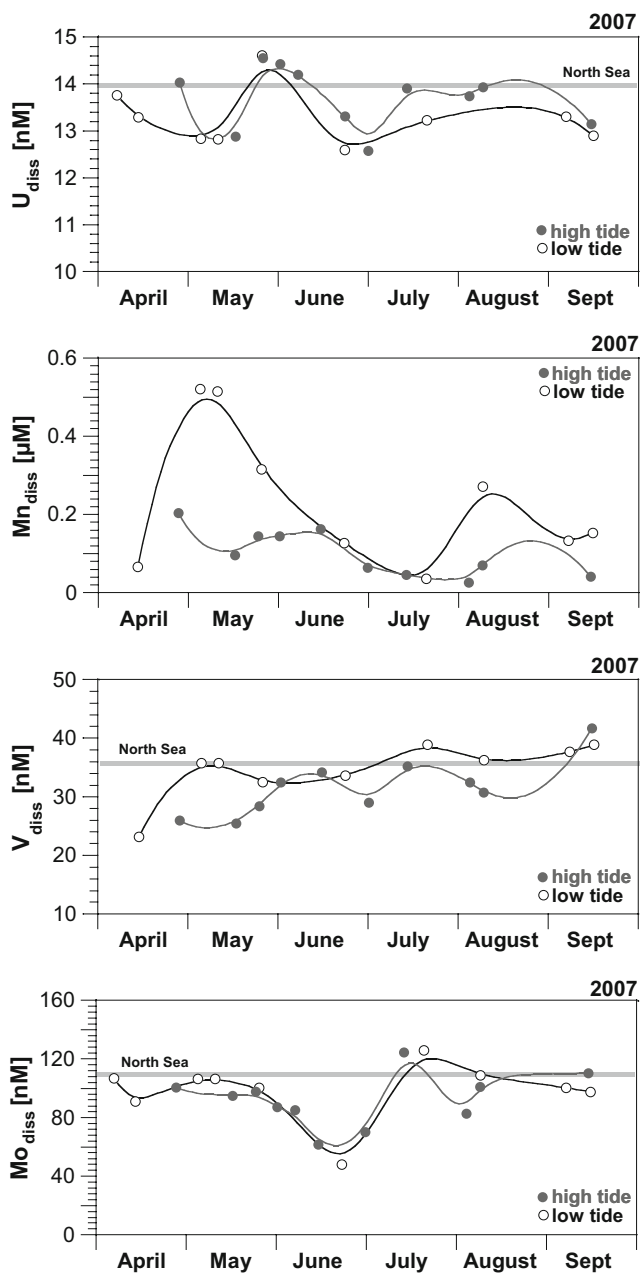


Fig. 6 Concentrations of dissolved U, Mn, V and Mo in the water column of the Spiekeroog Island backbarrier area from April to September 2007. The grey line denotes the North Sea value

al. (2002) showed that more than 40 % of reactive Fe is adsorbed to nearshore SPM. As a further source, Fe(III)-(oxi)hydr)oxides, which were formed in the surface sediments under oxic conditions in the winter months, are reduced when anoxic conditions reach the uppermost sediment layers in summer. Below a sediment depth of about 15 cm Fe²⁺ is effectively removed from the pore water throughout the year due to the reaction with sulphide. Especially in July and August this depth interval is highly enriched in sulphide (Fig. 8).

Phosphate, which is adsorbed to FeOOH as insoluble Fe (III)-phosphate complexes (Krom and Berner 1980; Matthiesen et al. 2001), is released together with Fe²⁺ which explains the high PO₄³⁺ enrichment in the pore water in September (Fig. 3a). Thus, within the water column, phosphate shows continuously increasing values after a significant depletion during the algae bloom in April and May (Fig. 9). In October, maximum values are reached which are almost 50% higher than concentrations before the algae bloom which is caused by PO₄³⁺ release from the sediment.

5.4 Manganese

Mn concentrations are more than an order of magnitude higher in the Wadden Sea than in the open North Sea or the North Atlantic (Tappin et al. 1995; Shiller 1997; Slomp et al. 1997; Dellwig et al. 2007b). In comparison to other trace metals, tidal and seasonal variations are most pronounced for Mn. During all cruises in 2002, a tidal cyclicity of Mn is visible with values being ca. five times higher during low tide compared to high tide. Seasonal differences were obvious with concentrations generally increasing from winter to summer by a factor of 10 (Fig. 10). Such elevated Mn levels have been almost exclusively explained by release from anoxic sediments during spring and summer while freshwater inputs may only contribute to certain amounts during high precipitation periods in autumn and winter (Dellwig et al. 2007a). However, considering the concentrations of Mn in pore waters and tidal creek waters (Fig. 5), the level of Mn released from the sediment is distinctly smaller when compared with the other trace metals. This difference can be attributed to oxidation effects close to the sediment–water interface leading to partial retention of Mn in the surface layer. Nevertheless, Mn values in tidal creek waters are still enriched when compared with the open water column (Fig. 10). For a more detailed description of the behaviour of Mn in the

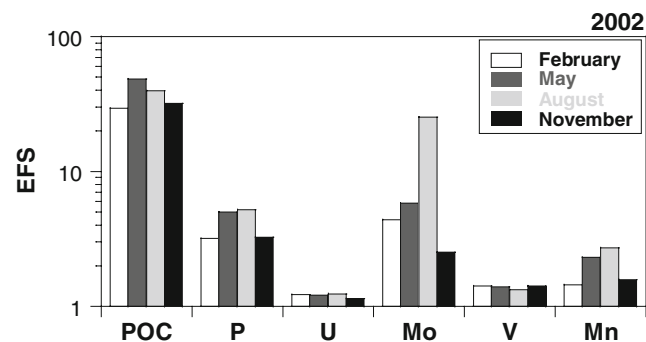


Fig. 7 Seasonal variation of enrichment factors (EFS) for particulate organic matter (POC), P, U, Mo, V and Mn of suspended particulate matter in 2002

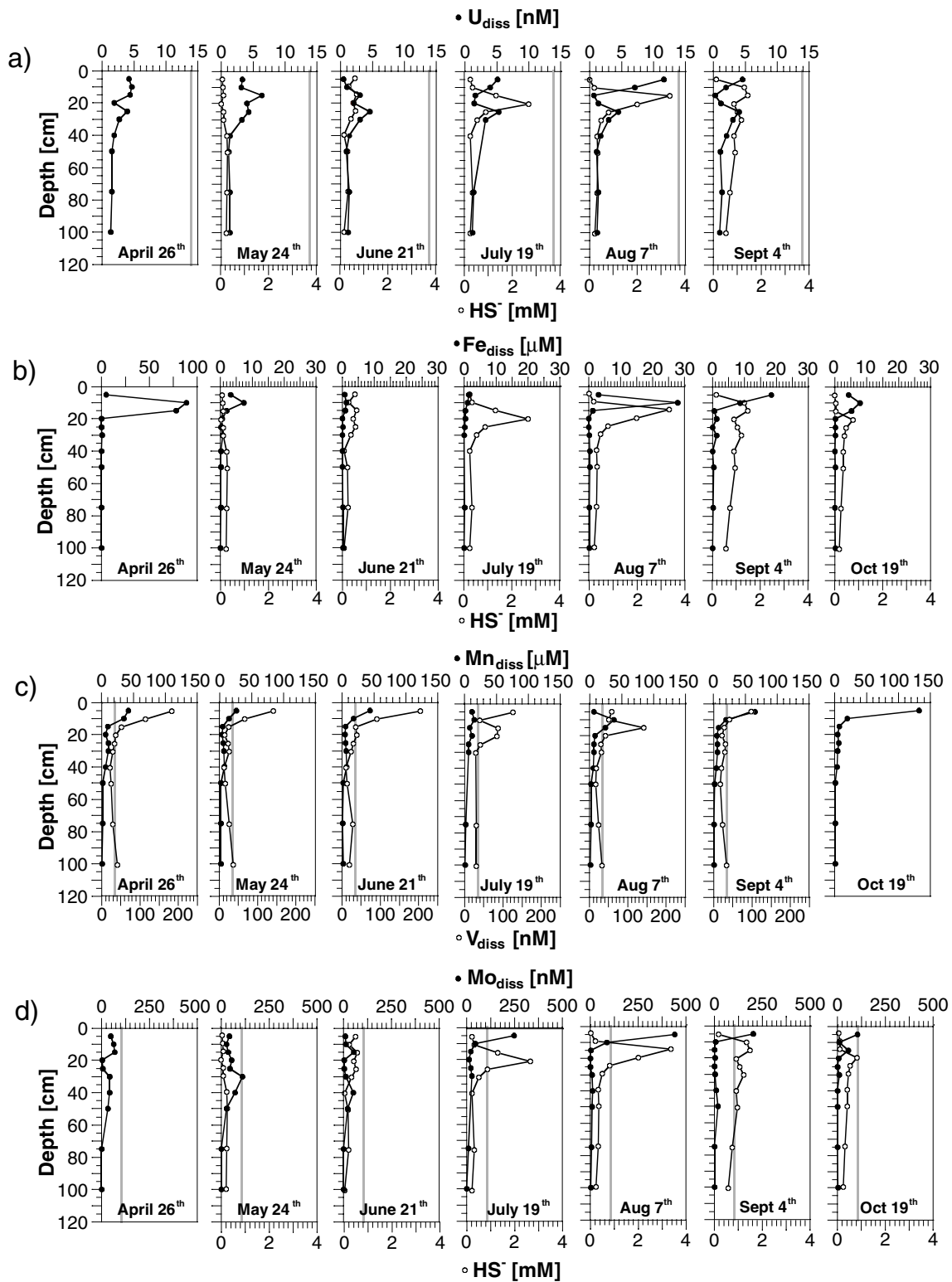


Fig. 8 Concentrations of dissolved **a** U and HS^- , **b** Fe (please note the different scale for Fe_{diss} in April) and HS^- , **c** Mn and V and **d** Mo and HS^- in the pore waters of site JS from April to October 2007. The *grey lines* mark the North Sea values of the trace metals

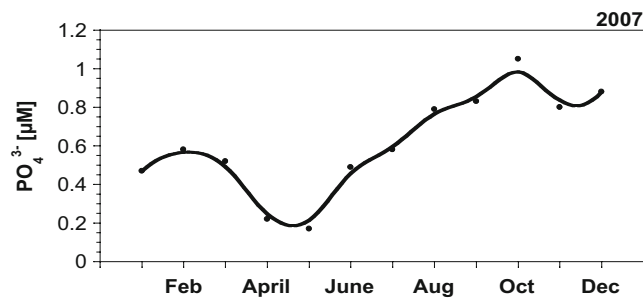


Fig. 9 Phosphate concentrations in the water column of the Spiekeroog Island backbarrier area in 2007 (monthly average)

study area, the authors refer to Dellwig et al. (2007a) and Bosselmann et al. (2003).

In the time series of 2007, the above-mentioned tidal differences are clearly visible with distinctly higher values at low tide (Fig. 6). Furthermore, seasonal variations are obvious especially at low tide with two maxima in April/May (max. 0.59 μM) and in August (max. 0.26 μM). Mn oxides precipitated at the sediment surface or freshly formed in the sediment during the winter months are reduced in spring and summer when the reduction zone for Mn(IV) moves upwards in the sediment leading to seasonal differences in the pore water composition.

From April to June, Mn²⁺ is enriched in the uppermost pore waters with values ranging from 26 to 44 μM at 5 cm depth (Fig. 8c). In July, dissolved manganese is depleted which is possibly caused by an exhaustion of the sediment in reducible Mn. The concentrations decrease to 12 μM at 5 cm depth (16 μM at 10 cm). This decrease is also obvious in surface water values (Fig. 6). From mid-June to beginning of August, a phase of depletion occurs with values around 0.07 μM at low tide. However, the water column already shows Mn depletion in June, whereas in the shallow pore waters, Mn²⁺ enrichment is still visible. Exhaustion of Mn²⁺ in the pore water is apparently not the only reason for Mn²⁺ depletion in the water column. In addition, elevated microbial Mn²⁺ oxidation in the water column may also cause depletion of dissolved Mn, thereby leading to enrichments of Mn on SPM (Nico et al. 2002). This hypothesis is confirmed by SPM data from 2002 which show a general increase of particulate Mn from winter towards summer (Fig. 7). Additionally, data from June 2007 (not shown) reveal a clear Mn enrichment with an EFS value of 2.5. Depletion in dissolved Mn may further be due to accumulation of Mn oxides by *Phaeocystis* sp. as reported by Lubbers et al. (1990). However, data of 2007 do not show a pronounced increase of *Phaeocystis* sp. cell numbers (Fig. 2) during the period of Mn²⁺ depletion.

In August, pore-water concentrations increase again to 38 μM (at 10 cm depth) and to 65 μM (at 5 cm depth) in September and finally reach a value of 132 μM (at 5 cm

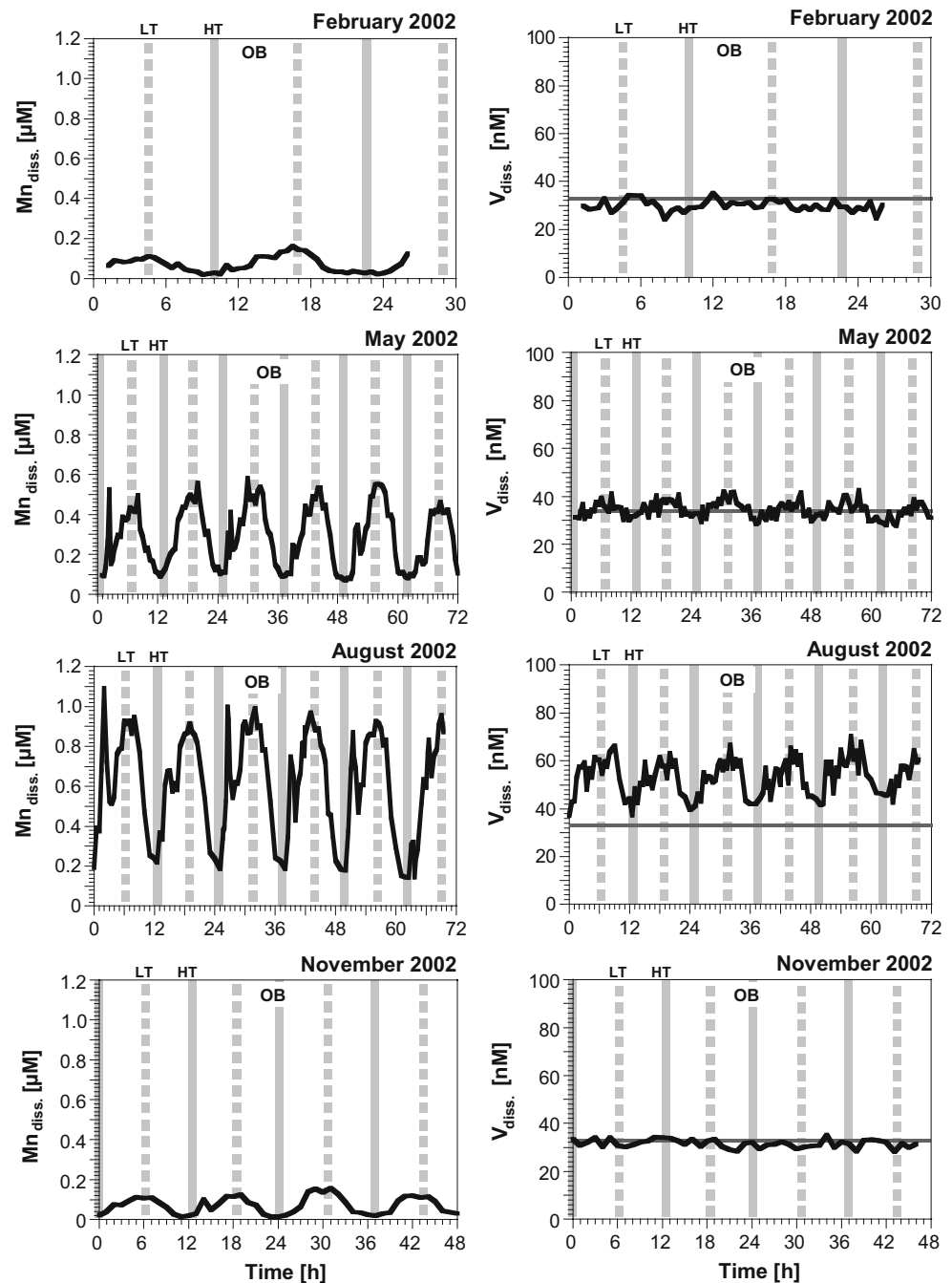
depth) in October. SPM data of August 2002 show a significant Mn enrichment (Fig. 7; Dellwig et al. 2007b) which is also confirmed by the data from 2007 showing a threefold Mn enrichment in August. After the summer algae bloom, Mn oxides are deposited along with organic-rich aggregates at the sediment surface replenishing the Mn reservoir in the sediment. Consequently, microbial reduction of Mn oxides leads to a significant release of Mn²⁺ into the pore water, followed by Mn²⁺ diffusion from the surface sediment into the open-water column, which causes an increasing Mn²⁺ level in the water column (Fig. 6).

5.5 Vanadium

During the Wadden Sea cruises in February and November 2002, dissolved V concentrations are close to the value in the North Atlantic (33–36 nM; Huizinga and Kester 1982; Middelburg et al. 1988). In contrast to dissolved Mo and U, tidal cyclicity is less pronounced for the winter samples (Fig. 10), as the freshwater, which is contributed to the Wadden Sea via the flood-gates in Neuharlingersiel, contains slightly higher levels of dissolved V (flood-gate in winter, 45 nM, Table 1). During spring and summer, a pronounced tidal cyclicity is obvious with elevated values during low tide especially in August 2002. Such increase requires an additional element source; thus, freshwater (flood-gate summer, 86 nM) as well as pore-water input have to be considered. Although the V concentration of freshwater is about twofold higher in summer, this source is insufficient to cause the observed vanadium increase in the surface waters of the backbarrier area (Dellwig et al. 2007b). Therefore, pore waters draining out of the sediments during low tide are the more likely source, as seen in Fig. 5, which shows elevated concentrations of V in pore water and tidal creek waters.

The similarity between the tidal patterns of V and Mn in spring and summer indicates a coupling of V to the Mn cycle although their redox chemistry is different (Fig. 10). Shiller and Mao (1999) reported a complex behaviour for V in two estuaries of the Louisiana shelf. The authors observed both the loss of V from open Gulf water to oxygen-depleted shelf sediments as well as release of V from the sediments. This initially contradictory finding was explained by up- and downward diffusion of V released from particles at the sediment surface. A similar process might be of importance for V enrichments in tidal creeks during summer. Oxidation of dissolved Mn and Fe in the water column of the Wadden Sea leads to the formation of oxy-hydroxide phases and concomitant scavenging of certain trace metals like Co, Mo and also V (e.g. Goldberg 1954; Craig 1974; Balistrieri et al. 1981). SPM does not show seasonal variations or significant V enrichment (Fig. 7) because the high geogenic background of V

Fig. 10 Seasonal variations of dissolved Mn and V in the water column of the Spiekeroog Island backbarrier area in 2002. The vertical grey line marks high tide (HT) and the dashed line low tide (LT). The horizontal grey lines in the V plots denote the North Atlantic value



($130 \mu\text{g g}^{-1}$ Wedepohl 1971) possibly covers influences caused by dissolved-particulate transfer reactions. When the particles impinge the tidal-flat sediment surface and reach the anoxic zone, oxyhydroxides are reduced and trace metals will be released to the pore water (e.g. Callender and Bowser 1980; Klinkhammer 1980; Klinkhammer et al. 1982; Sawlan and Murray 1983). A fraction of the released V may remain mobile due to complexation by organic ligands (Brumsack and Gieskes 1983) and may, therefore, be able to escape from the pore-water system into the water column via advective processes induced by the tides (Fig. 10).

In the 2007 time series, vanadium shows less significant variations with concentrations lying around the usual seawater level (Fig. 6). However, similarities to Mn are visible with maximum values in April/May followed by a slight depletion in May and June, which is possibly due to effective V scavenging by freshly formed Mn oxides. In July, V values exceed the North Sea value whereby V increases earlier than Mn, a relation which probably can be explained by processes in the pore water, e.g. V release from degraded organic matter (Szalay and Szilágyi 1967).

In the pore-water system, V shows highest concentrations in the uppermost centimetres of the sediment (Fig. 8c)

with values ranging between 165 and 204 nM from April to June, which is clearly above the seawater level. By contrast, in July, the concentrations start to decline in the top centimetres and decrease to a value of 57 nM in August. After this short depletion phase, V increases again and reaches a value of 93 nM in September, possibly caused by reduction of MnO_x phases as reported, for instance, by Morford et al. (2005).

However, a slight V enrichment in the pore water of the uppermost sediment is still visible in July while Mn is distinctly depleted. Therefore, a V release from organic matter is suggested for the enrichment. Cheshire et al. (1977) described vanadium binding in solid phase by sorption to organic substances. During organic matter degradation, vanadium is released, increasing the pore-water concentrations and finally the sea-water concentrations, which may explain the elevated V concentrations in the water column in July.

5.6 Molybdenum

Figure 4 presents the seasonal and tidal variability of dissolved Mo for the Wadden Sea cruises in 2002. Like U, dissolved Mo reveals a conservative tidal pattern in February 2002 with maximum concentrations at high tide when the influence of North Sea water is most pronounced. Again, a normalisation to a salinity of 35 psu leads to concentrations close to the North Atlantic value (Morris 1975) and smoothes tidal patterns. Conspicuous is the complete change in behaviour of Mo in August 2002 (Dellwig et al. 2007b), with Mo showing a tidal cyclicity with maximum values during low tide (Fig. 4). As a certain increase of dissolved Mo in tidal creek waters was also observed in August 2002 (Fig. 5), tidal-flat sediments have to be considered as a significant source. Such a process would imply less pronounced reducing conditions in the sediments, enabling the release of Mo due to oxidation of sulphidic compounds via tidal pumping. However, this is rather improbable due to the occurrence of partly anoxic sediment surfaces in the summer months. Therefore, a complexation with organic ligands is more likely to cause Mo stabilisation in this sulphidic environment.

Figure 6 shows the trend of Mo in the water column in 2007. From April to May, dissolved Mo shows conservative behaviour with values ranging between 92 and 107 nM at salinities between 30 and 32 psu. At the end of May, the Mo concentration starts to decrease until a minimum value of 49 nM is reached in June, without any changes in salinity. In the following time, a fast increase of Mo is observed which even exceeds the usual seawater level (107 nM, Morris 1975; Collier 1985) in July (126 nM, Fig. 6). Again a slight decrease to a value of 83 nM is seen at the beginning of August followed by a further increase to

100 nM (Fig. 6). These findings are in agreement with recently published results by Dellwig et al. (2007a). The authors observed a decrease in dissolved Mo down to 30 nM in the same area in 2005. During both years, this decrease in Mo coincided with collapsing algae blooms as deduced from the ratio of phaeopigments and chlorophyll *a* in 2005 (Dellwig et al. 2007a) and decreasing numbers of diatom cells parallel to increasing silica values in June 2007 (Fig. 2). During the spring bloom, no depletion was observed in 2005 and 2007 which emphasises the importance of bacterial activity. In spring, bacterial cell numbers are still as low as in the winter months and their activity is limited by lower temperatures. In contrast, elevated temperature in the summer months favours bacterial activity as seen in increasing numbers of bacteria cells (Dellwig et al. 2007a).

Assimilatory uptake of Mo by cyanobacteria (N_2 fixation) or phytoplankton (NO_3^- fixation) can be ruled out to cause such a distinct Mo decrease in the water column. Cyanobacteria do not occur in the water column of the study area and the diatom abundance is too low during the phase of Mo depletion due to breakdown of the diatom bloom. Furthermore, Mo uptake is inhibited by the high sulphate concentrations in the study area (Cole et al. 1986, 1993).

Scavenging of Mo during bacterial oxidation of Mn^{2+} may be an effective process for Mo removal (e.g. Berrang and Grill 1974; Barling and Anbar 2003; Wasylenki et al. 2008). This assumption is underlined by simultaneously increasing EFS values of Mo and Mn from winter to summer (Fig. 7). Dellwig et al. (2007a), on the other hand, did not observe a clear relation between the behaviour of Mo and Mn during detailed investigations in the study area in 2005. Therefore, the authors assumed fixation of Mo in oxygen-depleted micro-zones on aggregates, which are favoured by elevated microbial activity during breakdown of algae blooms. However, Ploug et al. (1997), for instance, did not observe any sulphide in anoxic areas of aggregates which is required for Mo fixation in aggregates. The authors assumed that short persistence of anoxic conditions limits slow-growing sulphate reducers.

Another possibility is the complexation by freshly formed organic matter during the breakdowns of summer phytoplankton blooms (Dellwig et al. 2007a). This assumption is supported by the fact that particulate matter is generally enriched in Mn during summer, whereas enrichments of Mo are only observed during time periods of high bioproductivity.

Furthermore, the formation of large areas with reduced sediment surfaces (Böttcher et al. 1999) may be a temporal and local sink for Mo in sulphidic sediments (Erickson and Helz 2000). This assumption is confirmed by data from 2002 showing significant Mo depletion ($\text{Mo}_{\text{diss.}}$ 29 nM) in

the water above such a sulphidic sediment surface. Nevertheless, an unusual expansion of reduced sediment surfaces as reported by Böttcher et al. (1999) was not observed during the investigation period.

The pore water generally shows Mo depletion compared to the usual seawater value (Fig. 8d). At depths below 50 cm, Mo is effectively removed from the dissolved phase by sulphide. After the Mo depletion in the water column, the Mo level increases significantly in the uppermost pore waters from 246 nM in July 2007 to a maximum value of 440 nM in August 2007, thus exceeding the seawater level by a factor of 4. In contrast, below a sediment depth of 10 to 15 cm, Mo still shows the typical depletion due to fixation in the presence of sulphide. Elevated Mo values in the pore waters may be caused by deposition and subsequent microbial mineralization of Mo-rich aggregates (Dellwig et al. 2007b). Additionally, reduction of Mn oxides from impinged aggregates can also cause release of formerly scavenged Mo. In September 2007, the Mo concentrations in the uppermost pore waters still have a value of 204 nM (Fig. 8d) although sulphide is present. The finding is probably due to sulphide concentration below the

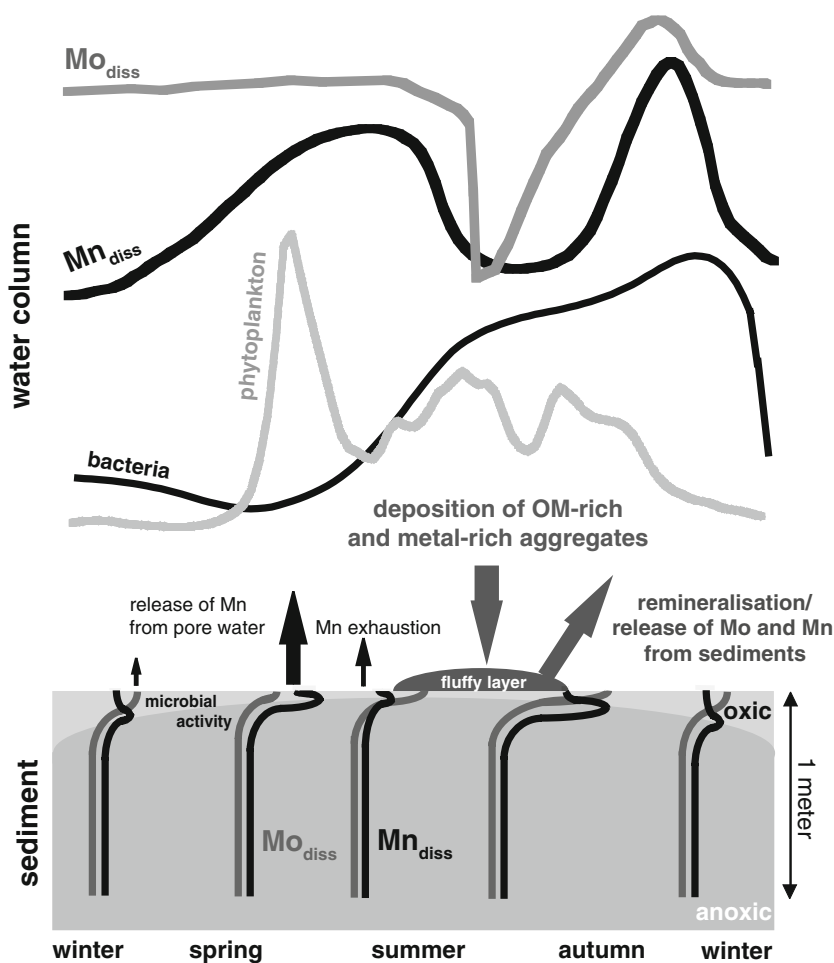
switching point between the geochemical states MoO_4^{2-} and MoS_4^{2-} , which was found by Erickson and Helz (2000) to be close to $11 \mu\text{M H}_2\text{S (aq.)}$. In October 2007, the Mo concentrations decrease to 104 nM reaching again the sea water value.

6 Conclusions

During sampling campaigns in 2002 and 2007, samples were taken from the open water column and from shallow pore waters of the backbarrier tidal flats of the island of Spiekeroog (Southern North Sea). It was the aim to investigate tidal and seasonal variations of the redox-sensitive trace metals Mn, Fe, Mo, U and V and their response to biological activity.

Water-column signatures of redox-sensitive trace metals (Mo, Mn, U and V) are significantly influenced by changes in bioproductivity. Pelagic and benthic coupling is triggered by enhanced biomass production in the open-water column. Organic matter produced during algae blooms is deposited via aggregates and incorporated into the sediments. In-

Fig. 11 Conceptual model (modified after Dellwig et al. 2007a) showing Mn and Mo dynamics in the water column and pore waters resulting from a pronounced benthic–pelagic coupling. Seasonal fluctuations of phytoplankton growth significantly influence the trace metal budget in the water column and shallow pore waters. Schematic water column trends and pore-water profiles illustrate the seasonal variations of Mn (black lines) and Mo (dark grey lines) dynamics due to pelagic and benthic coupling. The general pore-water trends are adapted to the scale of the present investigations



creasing microbial activity in summer leads to significant release of DOC, metabolites and trace metals during degradation of the aggregates. Most pronounced dynamics in the open-water column are seen for Mn showing maximum values during low tide when Mn-rich pore waters drain out of the sediments. Exhaustion and replenishing periods in the surface sediments cause distinct seasonal differences of the Mn level in the water column. V behaves similar to Mn due to scavenging by freshly formed MnO_x while U shows only slight water column depletion especially in summer, most likely due to fixation in anoxic sediments.

Non-conservative behaviour of Mo in the open-water column has been evidenced recurrently, after breakdown of summer algae blooms. It remains unclear whether this phenomenon is caused by scavenging of Mo by MnO_x , interactions with organic matter, and/or sedimentary uptake. However, Mo enrichments in shallow pore waters during summer indicate Mo removal from the water column and transfer into surface sediments.

This benthic–pelagic coupling of the investigated ecosystem is summarised in the conceptual model shown in Fig. 11. The model illustrates the behaviour of Mo and Mn in the water column and upper sediments as a response to biological, geochemical and sedimentological processes. Future investigations will have to consider benthic flux measurements to elucidate the quantitative impact of different processes on benthic–pelagic coupling. The determination of exchange rates will show the importance of Wadden Sea sediments as temporal trace metal sources or sinks.

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