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A comparative study of manganese dynamics in the water column and sediments of intertidal systems of the North Sea

Nicole Kowalski [a,*], Olaf Dellwig [a], Melanie Beck [b], Maik Grunwald [b,c], Claus-Dieter Dürselen [d], Thomas H. Badewien [b], Hans-Jürgen Brumsack [b], Justus E.E. van Beusekom [e], Michael E. Böttcher [a]

[a] Leibniz Institute for Baltic Sea Research (IOW), Geochemistry and Isotope Geochemistry Group, Marine Geology Section, Seestraße 15, D-18119 Warnemünde, Germany
[b] Institute for Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany
[c] Helmholtz-Zentrum Geesthacht, Zentrum für Material- und Küstenforschung, Max-Planck-Str. 1, D-21502 Geesthacht, Germany
[d] AquaEcology GmbH and Co. KG, Marie-Curie-Straße 1, 26129 Oldenburg, Germany
[e] Alfred-Wegener-Institute for Polar and Marine Research, Wadden Sea Station Sylt, Hafenstraße 43, D-25992 List, Germany

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ABSTRACT

The dynamics of the redox-sensitive trace metal manganese (Mn) and its response to biological activity were investigated in the water column and shallow pore waters of the German Wadden Sea (southern North Sea) in 2008 and 2009. Two systems, one from the southern (backbarrier area of Spiekeroog Island) and one from the eastern part (Sylt-Rømø Wadden Sea) of the German Bight were compared. The major aim was to examine to which extent biogeochemical findings are specific for a particular tidal basin or transferable to other basins of the German Wadden Sea.

Although both study areas reveal hydrodynamical, sedimentological, and ecological differences, qualitatively pronounced similarities in Mn dynamics are observed. Thus, complex cycling of dissolved Mn with increasing values in spring and late summer due to elevated biological activity as well as a depletion period in early summer were observed in both study areas. This finding suggests a seasonal behaviour of Mn being generally representative for the tidal basins of the southern North Sea. Quantitative differences are significant as the backbarrier area of Spiekeroog Island shows much higher concentrations of dissolved Mn in the water column especially during spring. We suggest that this difference is due to a larger sediment area/water volume ratio in the Spiekeroog backbarrier area combined with a higher release of dissolved Mn from the tidal flat sediments as seen in pore water profiles from surface sediments.

Site-specific differences are also seen in further tidal systems of the North Frisian Wadden Sea, which are characterised by individual hydrodynamical and sedimentological conditions. Several transects leading from offshore locations towards the coast also revealed a highly variable Mn level. Overall, the North Frisian Wadden Sea most likely represents a less important source for dissolved Mn than the East Frisian Wadden Sea. Furthermore, our data suggest that site-specific properties of the different tidal basins have to be considered in budget calculations for the entire Wadden Sea.

1. Introduction

The tidal flats of the German Wadden Sea are highly productive areas which results in intense element cycling (e.g. Brockmann et al., 1990; De Jonge et al., 1996; Boudreau et al., 1999). Separated by barrier islands, the tidal flats are connected with the North Sea by tidal channels, which enable water and material exchange. Enhanced productivity is due to high nutrient availability via (a) river discharge (e.g. Van der Veer et al., 1989; Brockmann et al., 1996, 1999a,b; Van Beusekom et al., 2001), (b) organic matter import from the North Sea (Van Beusekom et al., 2001; Van Beusekom and de Jonge, 2002), and (c) release from tidal flat sediments during organic matter turnover and nutrient remineralization (Slomp et al., 1998; Van Beusekom et al., 1999).

The productivity shows a pronounced seasonal dependency with highest biomass production in the summer months (Van Beusekom et al., 2001). Enhanced input of organic material to the tidal flat sediments during breakdown of phytoplankton blooms leads to elevated biological activity in surface sediments (Böttcher et al., 1999). During mineralization the metabolites are released to the

* Corresponding author.
E-mail address: nicole.kowalski@io-warnemuende.de (N. Kowalski).

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pore water and may subsequently be transported to the water column by diffusion or advection (Sundby et al., 1992; Van Raaphorst et al., 1993; Huettel et al., 1998; Slomp et al., 1998; Van Beusekom et al., 1999; Beck et al., 2008a; Grunwald et al., 2010). Directly or indirectly coupled to mineralization processes reduction of Mn oxides leads to fluxes of Mn^{2+} across the sediment–water interface (e.g. Balzer, 1982; Sundby and Silverberg, 1985; Slomp et al., 1997).

In this way, the so-called "bio-reactor" Wadden Sea acts as an important source for the open North Sea in terms of recycled nutrients (Van Raaphorst and van der Veer, 1990; Dick et al., 1999; Grunwald et al., 2010), dissolved inorganic carbon (Brasse et al., 1999; Böttcher et al., 2007; Thomas et al., 2009), and methane (Grunwald et al., 2009).

Elevated biological productivity in coastal waters influences the transformation of redox-sensitive trace metals revealing their importance as probable indicators for benthic–pelagic coupling. Schoemann et al. (1998), Muller et al. (2005), Dellwig et al. (2007a,b) and Kowalski et al. (2009) investigated manganese (Mn) dynamics in coastal waters and suggested a tight relationship between Mn dynamics in the water column and phytoplankton blooms. The increasing supply of freshly formed organic matter, in combination with rising temperatures, induces enhanced microbial activity in the surface sediments (Böttcher et al., 2000, 2004; Musat et al., 2006; Al-Raei et al., 2009). As a consequence anoxic conditions extend to the surface sediments leading to the reduction of Mn oxides (e.g., Burdige and Nealson, 1986), and pronounced Mn^{2+} release in spring and summer months. Such a seasonal behaviour of Mn in surface sediments of coastal areas was also reported by Aller and Benninger (1981), Aller (1994), Skowronek et al. (1994), and Bosselmann et al. (2003). This release of dissolved Mn from the sediments appears to be responsible for a 10-fold increase in the concentrations of dissolved Mn in the water column from winter to summer (Dellwig et al, 2007a). However, further investigations revealed a more complex behaviour of Mn in the water column during the summer months as indicated by periods of depletion and replenishment of the Mn pool in the surface sediments of intertidal sand flats (Dellwig et al., 2007b; Kowalski et al., 2009).

As the Mn concentrations are distinctly higher in the Wadden Sea, the intertidal systems may represent an important Mn source contributing significantly to the Mn budget of the North Sea (Slomp et al., 1997; Dellwig et al., 2007b). However, such budget estimations require detailed knowledge about the seasonal Mn dynamics.

Long-term measurements of nutrients and phytoplankton previously demonstrated significant differences in the biogeochemistry and ecology of the southern and northern coastal areas of the North Sea (Uhlig and Sahling, 1990; Elbrächter et al., 1994; Van Beusekom et al., 2009a). Van Beusekom et al. (2009a) suggested higher eutrophication in the East Frisian Wadden Sea because of higher biomass production in summer and nutrient concentrations in autumn compared to the North Frisian Wadden Sea. Different levels of eutrophication may also impact the biogeochemical Mn cycle and magnitudes of fluxes in the different tidal areas of the German Bight.

Furthermore, different sedimentological and hydrodynamical conditions may also affect Mn cycling. For instance, Bosselmann et al. (2003) and Al-Raei et al. (2009) showed that the intensity of anaerobic degradation processes in the surface sediments and thus the nutrient and trace metal release depend on the sediment type. Exchange processes across the sediment–water interface is more efficient in permeable sediments due to the impact of advective pore water transport and sediment resuspension, whereas element transport in pore waters of mud flat sediments is more controlled by diffusion and bioturbation (e.g., Huettel et al., 1998; Boudreau et al., 1999; Aller, 2001, 2004; Shaw, 2003a; Billerbeck et al., 2006; Franke et al., 2006).

The aim of the present study was to compare annual biogeochemical Mn dynamics in tidal flat areas of the East and North Frisian Wadden Sea. This is of particular importance as the representativity of datasets from specific sites used to estimate Mn budgets of the entire Wadden Sea and the North Sea is still not known. Therefore, seasonal investigations of dissolved and particulate Mn, phytoplankton, and nutrient dynamics were conducted in the backbarrier area of Spiekeroog Island as part of the East Frisian Wadden Sea and in four tidal flat areas of the North Frisian Wadden Sea.

2. Study areas

The backbarrier tidal flats of Spiekeroog Island (Fig. 1A) cover an area of 74 km^2 (intertidal flat area ca. 30 km^2, Walther, 1972) and are characterised by semi-diurnal tides and a mean tidal range of 2.6 m (Flemming and Davis, 1994). The mean water volume is 145×10^6 m^3 at high tide (40×10^6 m^3 at low tide; Lübben et al., 2009). Water exchange with the open North Sea occurs via the major tidal channel (Otzumer Balje) between the islands of Langeoog and Spiekeroog and amounts to one-third of the tidal prism per tidal cycle (Shaw, 2003b; tidal prism ca. 105×10^6 m^3, 72% of the entire water volume, Stanev et al., 2003). The backbarrier area shows a sediment distribution typical for mesotidal areas with a dominance of sandy sediments and decreasing grain size towards the mainland due to lower current velocities which favour deposition of finer particles (e.g. Postma, 1961; Reineck et al., 1986; Flemming and Davis, 1994). The occurrence of small mixed or mud flat areas in the centre is due to biodeposited mud in and around mussel banks (Flemming and Davis, 1994).

The Sylt-Rømø Wadden Sea (Fig. 1B) is a semi-enclosed bight encompassing an area of 407 km^2 (intertidal flat area 135 km^2), which is distinctly larger than the backbarrier area of Spiekeroog Island. The water volume is 1120×10^6 m^3 (570×10^6 m^3 at low tide). The tides are semi-diurnal and the mean tidal range is about 2 m. Tidal water transport (550×10^6 m^3, 49% of the entire water volume) occurs via three main tidal channels joining into a single tidal inlet between Sylt and Rømø Island (Gätje and Reise, 1998). The tidal flat area in the north of Sylt Island is influenced by aeolian input of medium sand originating from dunes and the western beach area of Sylt Island. This leads to a coarsening of sediments in the marginal area while the central parts consist of fine-grained sediments. The tidal flats of Rømø Island are dominated by muddy sediments (Bayerl et al., 1998).

Contrasting to the Sylt-Rømø bight, the North Frisian tidal basins of Hörnum Deep (Fig. 1(A) (2)) and Norderaue (3) are characterised by an intense exchange with the neighbouring tidal flats (Dick and Schönfeld, 1996). The northern part of the tidal flats of the Hörnum Deep is artificially bordered by the Hindenburg dam favouring accumulation of fine-grained muddy sediments (Wohlenberg, 1954). In the Norderaue, mixed and mud flats occur close to the coast and at the lee sides of the Islands Amrum, Föhr and Langeness (Stock et al., 1996). The areas of the Outer and Inner Eider (4) form the estuary of the Eider River being separated by a flood-gate. The freshwater contributions by the Eider River are on average 0.9×10^9 m^3 y^{-1} (Essink et al., 2005).

3. Materials and methods

3.1. Sampling

Samples of seawater and suspended particulate matter (SPM) from surface waters were collected using R/V "Navicula" (Carl von Ossietzky University, Oldenburg), R/V "Mya" (AWI Sylt), and R/V "Südfall" (FTZ Büsum). Surface water samples were taken close to low tide (±1.5 h) in the tidal inlet between the Islands of Spiekeroog and Langeoog (Otzumer Balje, OB) at a time series station located at