

## IRON-SULFUR-MANGANESE DYNAMICS IN INTERTIDAL SURFACE SEDIMENTS OF THE NORTH SEA

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### Introduction

In coastal marine sediments the decomposition of organic matter is catalyzed by microorganisms using oxygen, nitrate, manganese and iron(oxyhydr)oxides and sulfate as the terminal electron acceptors (e. g., FROELICH *et al.*, 1979; JØRGENSEN, 2000). Up to more than 50% of the oxidation processes are related to microbial sulfate reduction. A number of complex microbial and non-biological reactions typically takes place in marine surface sediments. Intertidal surface sediments are the ideal sites to study the influence of dynamic boundary conditions on early diagenetic biogeochemical element transformations and their impact on the element transfers across the sediment-water interface.

The present study concentrates on the dynamic reactions within the coupled biogeochemical cycles of oxygen, manganese, iron and sulfur in different intertidal surface sediments on a seasonal basis. The main purpose was to increase our understanding of element dynamics and their relation to factors like, e. g., sediment type (and corresponding organic matter and metal load), temperature, and hydrodynamics.

The main interest was in the factors controlling the dynamics of manganese, iron and sulfur in different types of intertidal sediments. During early diagenesis, manganese(IV) and iron(III)(oxyhydr)oxides can be reduced and recirculated through various redox processes (e. g., THAMDRUP *et al.*, 1994; CANFIELD *et al.*, 1993) and are, therefore, important for material and energy flow. Measurements were carried out to investigate the dynamics of biogeochemical reactions within the coupled sedimentary oxygen, sulfur, carbon, manganese and iron cycles on the time scales of tidal cycles, day-night changes and seasons. The investigations were carried out in the field (*in situ*) as well as by laboratory incubations. Sediment cores and interstitial waters were typically analyzed down to about 20 cm depth.

### Study areas

The study areas are located in the German Wadden Sea (southern North Sea; Fig. 1). Whereas the sites for the investigation of intertidal sand and mixed flats are located in the backbarrier tidal area of Spiekeroog Island, mud flats were studied in the near-by Jade Bay (Site Dangast; BÖTTCHER *et al.*, 2000; LLOBET-BROSSA *et al.*, 2002). Sites Neuharlingersiel and Janssand represent intertidal mixed and sandy sediments, respectively. These different sampling sites were chosen to include a range of sediments with different sedimentological and geochemical properties (grain size, organic matter and metal content, permeability and porosity) and biological activities.

### Methods

Short sediment cores were taken during low and high tide and typically analyzed down to about 20 cm depth for a number parameters. Temperature profiles were measured *in situ* at different times to characterize temporal and spatial dynamics of temperature during the sampling period. Sediments were characterized for TOC and water contents. Pore waters were separated from the sectioned sediments by centrifugation under inert gas and (for parallel high-resolution measure-

ments of dissolved Fe and Mn) using DET and DGT gel samplers (e. g., ZHANG & DAVISON, 1999).

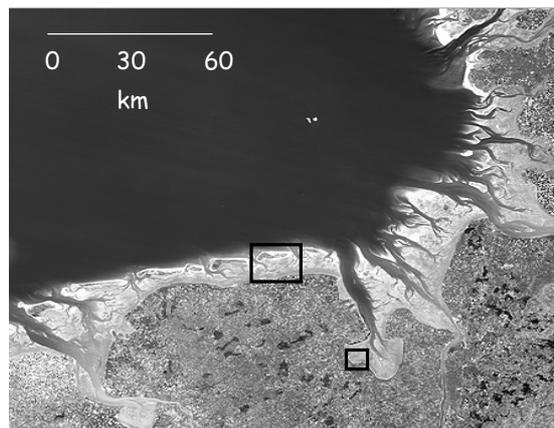


Fig. 1. Study areas in the German Wadden Sea (southern North Sea).

Additionally, pore waters were analyzed *in situ* for O<sub>2</sub>, pH, and H<sub>2</sub>S in high depth resolution using microelectrodes attached to autonomous lander systems (WALPERSDORF *et al.*, this volume). Spectral photometry and ICP-OES/MS were used to measure dissolved iron and manganese. Reactive iron and manganese pools were quantified by extraction using buffered Na-dithionite solution or HCl (THAMDRUP *et al.*, 1994). Different dissolved and solid sulfur fractions were quantified as, e. g., acid volatile sulfide (AVS, essentially FeS) and chromium reducible sulfur (CRS, mostly pyrite, FeS<sub>2</sub>, with minor elemental sulfur) by a two-step-distillation method and isotopically (<sup>34</sup>S/<sup>32</sup>S) characterized by means of C-irmMS. Pore water sulfate was quantified gravimetrically. Hydrogen sulfide was measured photometrically according to CLINE (1969) and with ion-sensitive electrodes. Microbial sulfate reduction rates were measured by the whole-core <sup>35</sup>SO<sub>4</sub><sup>2-</sup> tracer incubation technique (FOSSING & JØRGENSEN, 1989). The spatial distribution of the activity of sulfate-reducing bacteria was visualised by using the application of a newly developed *in-situ* monitoring technique ('2D-SRR-photo-emulsion-monitoring technique'; BÖTTCHER *et al.*, in prep.) which is based on the dark *in-situ* fixation of biogenic hydrogen sulfide with silver in photographic paper inserted within a tube. Benthic chambers (HUETTEL & GUST, 1992) were used to investigate the dynamics of metals and nutrients at the sediment-water interface.

### Results and discussion

Sampling sites include a range of sediments with different grain sizes, organic matter and metal (Fe, Mn) content and permeability, reflecting different hydrodynamic regimes. The study focuses on the seasonal dynamics of biogeochemical reactions in the C-S-Fe-Mn cycles. Figs. 2 and 3 show that the sulfur cycling is closely coupled to the reduction potential for metal (oxyhydr)oxides. The microbial production of hydrogen sulfide leads to the mobilization of iron and manganese. At the mixed flat site, the microsensor demonstrated a maximum oxygen penetration depth of about 5 mm. The development of a suboxic zone with a lack of accumulated hydrogen sulfide despite a maximum in bacterial sulfate reduction within the first cm of the sediment, and the accumulation of dissolved Fe(II) and Mn(II) may be attributed to the microbial reoxidation of sulfide and/or the reaction with metal(oxyhydr)oxides (BÖTTCHER *et al.*, 2000; LLOBET-BROSSA *et al.*, 1999). A maximum in AVS found during spring time (Fig. 3) coincides with a maximum in total SRR. Similar developments of zones with suboxic conditions were found for the mixed and the mud flat sites. The maximum concentration of dissolved iron below the depletion of sulfate reduction is compatible with the decline of hydrogen sulfide at this depth.

At the sandy site, reactions depend on the availability of substrates (e. g., BÖTTCHER *et al.*, 1998; HUETTEL *et al.*, 1998) and are more influenced by pore water and sediment (hydro)dynamics (HUETTEL *et al.*, 1998).

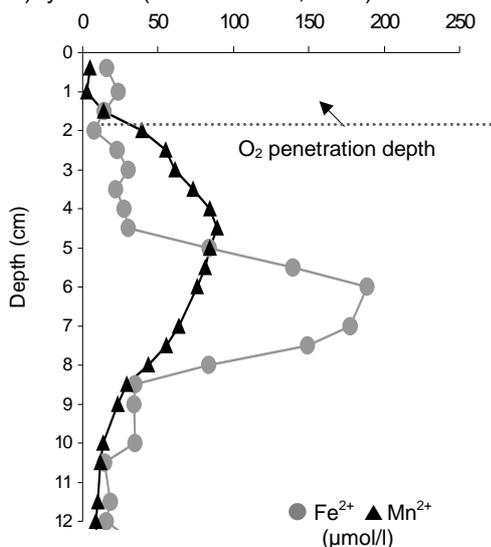


Fig. 2. Mixed flat during spring time. Porewater DET profiles of dissolved iron (●) and manganese (▲). Maximum depth 12 cm.

Within the sediment, the oxygen concentrations decreased below about half a millimeter (Fig. 4). The diffusive boundary layer had a thickness of about one millimeter and plays an important role for the exchange and reoxidation of solutes across the sediment-water interface (e. g., JØRGENSEN, 2000). The oxygen penetration depth is influenced by the oxygen concentration in the water column, photosynthesis, the activity of benthic organisms, and tidal hydrodynamics.

Fig. 4 shows that the activity of benthic microorganisms at day-time induced an increase of oxygen in the surface layer of the sediment. At night-time we measured lower oxygen concentrations in surface water due to lower temperatures, and the consumption below the surface.

Cycling of manganese and iron is important for the electron transfer. Reduced  $Fe^{2+}$  and  $Mn^{2+}$  diffuse to the sediment surface and are re-oxidized and precipitated again as metal (oxyhydr)oxides. Dissolved manganese is less sensitive to reoxidation than ferrous iron and, therefore, can partly be transferred across the sediment-water interface into the bottom waters. Experiments with benthic flux chambers demonstrate that dissolved manganese is able to escape the sediment and may be re-oxidized and -precipitated in the water column. Fig. 5 shows the range of the dissolved manganese concentration measured during short-time incubations using light and dark chambers.

At both sites where benthic chambers were applied (mixed and sand flat) higher concentrations of dissolved manganese were measured under dark conditions compared to the transparent set-up, indicating a light-dependent preferential removal of Mn(II) in the surface waters. Seasonal changes in the manganese retention capacity were found for the mud flat site (BÖTTCHER & HESPENHEIDE, unpublished; Fig. 6) indicating a coupling with the temperature-dependent overall microbial activity. The depth-integrated activity of sulfate-reducing bacteria shows seasonal variations typically with a maximum during summer due to changes in temperature and (at the sandy site) availability of organic matter.

Using the 2D-monitoring technique, the spatial distribution of bacterial sulfate reduction was investigated in permeable sandy and mixed sediments. Fig. 7 compares the gross bacterial sulfate reduction rates measured using radiotracers with the structure developed by the reaction of silver and biogenic hydrogen sulfide in an inserted photographic paper device.

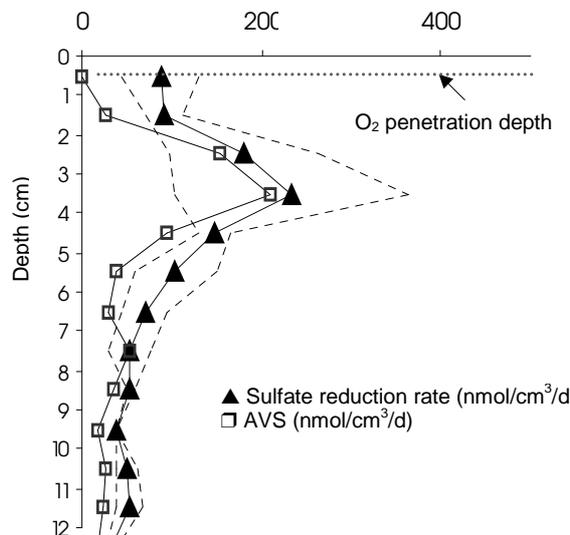


Fig. 3. Mixed flat during spring. (▲) Range of gross microbial sulfate reduction rates and the rate of  $H_2S$  produced and fixed in AVS (□). Max. depth: 12 cm.

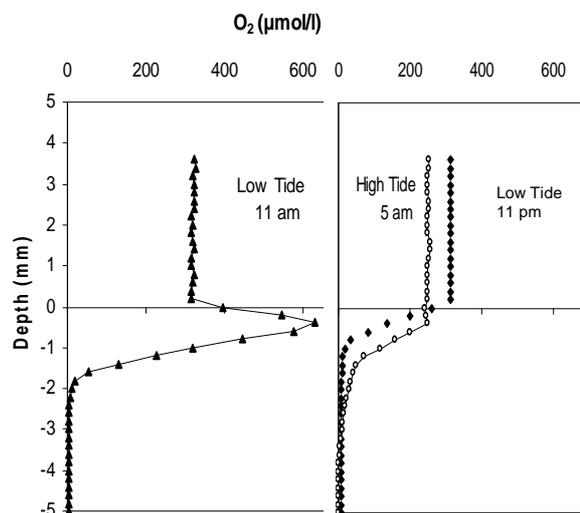


Fig. 4.  $O_2$  measurements during spring (mixed flat).

Due to the typically low organic matter contents sulfate reduction rates in the sandy sediments from Janssand are lower compared to the mixed sediment at Neuharlingersiel. Fig. 7 (right) gives a two-dimensional picture of the *in-situ* microbial hydrogen sulfide production. A zonation with relatively homogeneous vertical distribution of bacterial activity was found in the permeable sediment. This indicates a horizontally homogeneous distribution of substrates, sulfate-reducing bacteria and related biogeochemical processes. The activity in the mixed flat, on the other hand, is also vertically zoned, but shows 'hot and cold zones' probably due to zones of enhanced availability of substrate and textural effects resulting from the activity of benthic organisms.

The microbial dissimilatory sulfate reduction led to a significant discrimination of  $^{34}S$  and  $^{32}S$  between the inorganic sulfur fractions (AVS, pyrite) and dissolved porewater sulfate (Fig. 8). The magnitude of isotope discrimination indicates the dominant influence of microbial sulfate reduction with a superposition of reactions from the oxidative part of the sulfur cycle, including the formation and bacterial disproportionation of sulfur intermediates. Whereas AVS and  $SO_4^{2-}$  mainly reflect bacterial metabolism, the pyrite composition is additionally influenced by physical mixing processes. The oxygen isotopic composition of dissolved sulfate is out of isotope exchange equilibrium with seawater in the water column and at the

sediment-water interface. The downcore increase of  $^{18}\text{O}/^{16}\text{O}$  ratios in the mud and mixed sediments demonstrates the dominant control by bacterial sulfate reduction superimposed by the oxidative parts of the sulfur cycle.

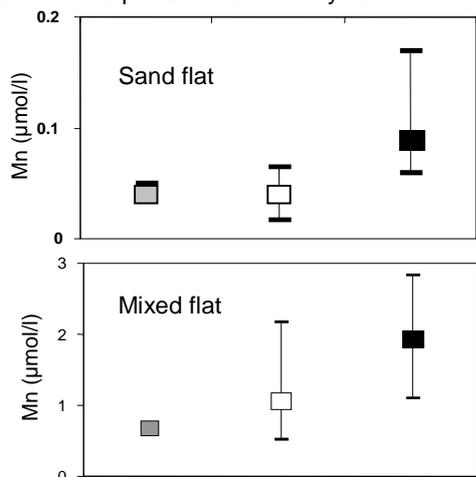


Fig. 5. Average concentration and the total range of liberated dissolved manganese during incubations in summer.

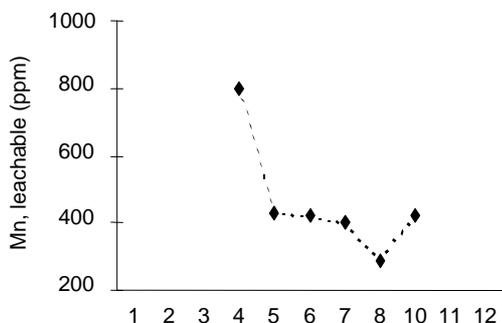


Fig. 6. Seasonal changes of  $\text{MnO}_2$  in the upper 5 mm of mud flat sediment (BÖTTCHER & HESPENHEIDE, UNPUBLISHED).

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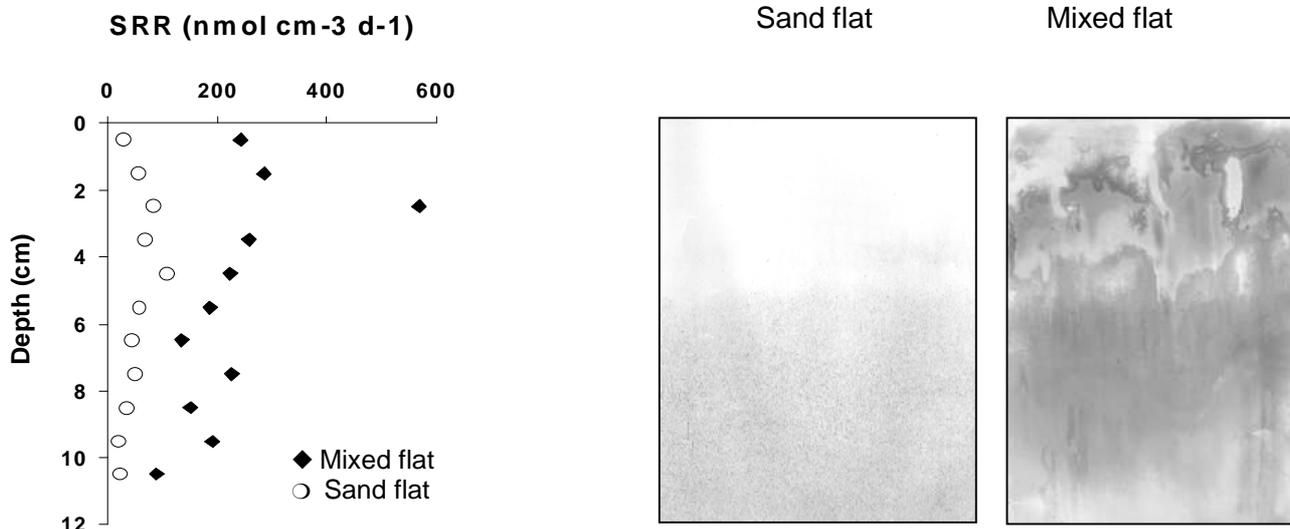


Fig. 7. Microbial sulfate reduction rates in sandy and mixed sediments (Janssand, Neuharlingersiel). Left: Whole core incubation technique with radiotracers. Right: Spatial distribution of zones of SRR monitored by the 2D-photoemulsion-monitoring technique.

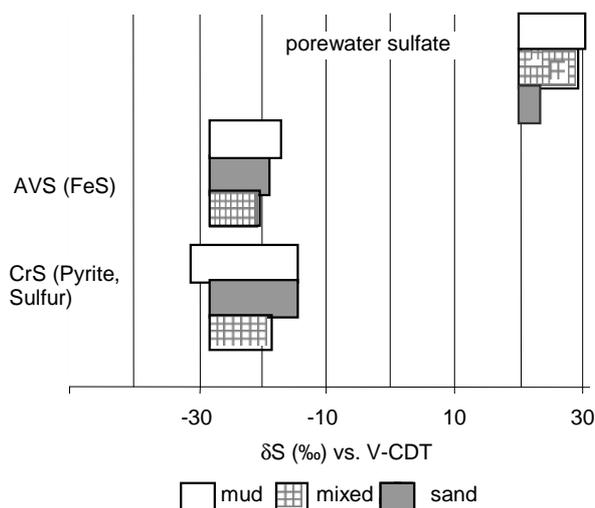


Fig. 8. Stable sulfur isotope discrimination between sulfate and the CRS and AVS fractions.

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## LIVING EVERY DAY WITH NOAH'S FLOOD: ELEMENT DYNAMICS IN INTERTIDAL SURFACE SEDIMENTS OF THE NORTH SEA

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### Introduction

In coastal zones, organic matter is degraded mainly within the sediment. Under steady-state conditions the microbially mediated reactions of organic matter oxidation proceed *via* a cascade using oxygen, nitrate, manganese and iron(oxhydr)oxides, sulfate and carbon dioxide/acetate as terminal electron acceptors. The spatial and temporal importance of the different processes in dynamic intertidal sediments is influenced by a number of different factors like the availability of organic matter, the bacterial community structure, the activity of benthic organisms, hydrodynamics, and temperature. The quantitative relationships and their spatial and temporal dynamics are still not fully understood.

Therefore, the biogeochemistry of organic matter mineralization is studied in temperate intertidal sediments of the German Wadden Sea (southern North Sea). Sampling sites (see BOSSELMANN *et al.*, this issue, for a map) were chosen to include a range of sediments with different grain sizes, organic matter and metal (iron, manganese) contents, and permeability, reflecting different hydrodynamic regimes. Sediment types ranged from sand to mud flats. Sands have previously been thought to harbor less microbial activity than silt- and clay-rich sediments because of the typically low organic matter contents and microbial cell numbers.

Our goal was to determine the major microbial degradation activities, as presented in Fig. 1, of intertidal sand plates in comparison to sediments with higher mud contents. The study focuses on the seasonal dynamics of the biogeochemical reactions in the coupled element cycles involving oxygen,

carbon, sulfur, iron, and manganese and the relationship to the sedimentary microbial community structure. To gain more insight into the importance of different microbially mediated and abiological reactions on dynamic sulfur cycling in a modern coastal environment, seasonal variations of stable isotope discrimination (S, O, C) in different oxidized and reduced sulfur and carbon species were also included. Measurements were carried out to investigate the dynamics on the time scales of tidal cycles, day-night changes and seasons. Special attention was paid to the influence of temperature, organic matter load, and bacterial abundances as process-controlling variables on element cycling in the surface sediments. Field results on seasonality are compared to laboratory and *in-situ* experiments. We report here on the results for sandy and muddy sediments. The methods for *in situ* measurements and assessment of microbial conversion rates as well as the study sites in the backbarrier tidal area of Spiekeroog Island (Janssand and Neuharlingersiel) and the Jade Bay (Dangast) are described in the publications of BOSSELMANN *et al.* (this issue), WALPERSDORF *et al.* (this issue) and WERNER *et al.* (this issue). For a comparison of different intertidal settings, we have included intertidal sandy sediments from locations near Westerhever and Königshafen.

### Results and discussion

In permeable sandy sediments, the flux of organic material and electron acceptors from the overlaying seawater and their transport and transformation within the sediment usually determines benthic conversion rates. In fine-grained silts and clayey sediments transport is often diffusional, whereas in coarse sediments advection is the dominant transport process. Advection in sediments is driven by the hydrodynamics of the overlaying water body, i. e. by currents over ripples and by wave action, as well as by burrowing macrofauna. Intertidal sand plates are exposed to tides, inducing further enhancement of advective transport. Our results show that the microbial activity in sands, when compared to muddy sediments, has been underestimated and that sands are significant in the element cycling in coastal zones by intense aerobic and anaerobic mineralization of organic matter. Due to the open system nature of permeable surface sands, they react more directly to dynamic changes of boundary conditions like hydrodynamics or local organic matter burial.

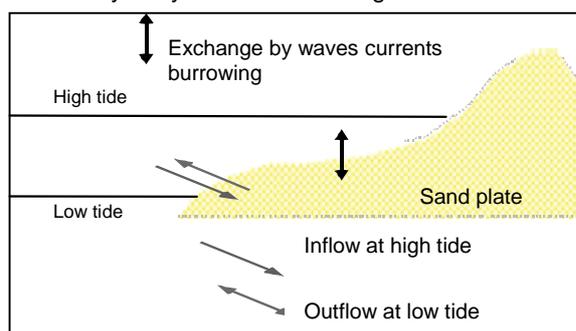


Fig. 1. Sketch of the main advection phenomena on intertidal sand plates.

Intertidal plates are exposed to a complex combination of variable environmental factors, such as tides, currents, air-exposure, storms, light and temperature. This strongly complicates assessment of the actual conversion rates in these sediments, as retrieved samples are no longer exposed to the field conditions and transport rates of oxygen and organics are different. Therefore, transport and conversion rates are best determined *in situ*. The highly dynamic nature of the environment and restricted accessibility during the tidal cycles complicates *in-situ* studies of intertidal areas. However, also equipment for *in-situ* measurements may change the hydro-