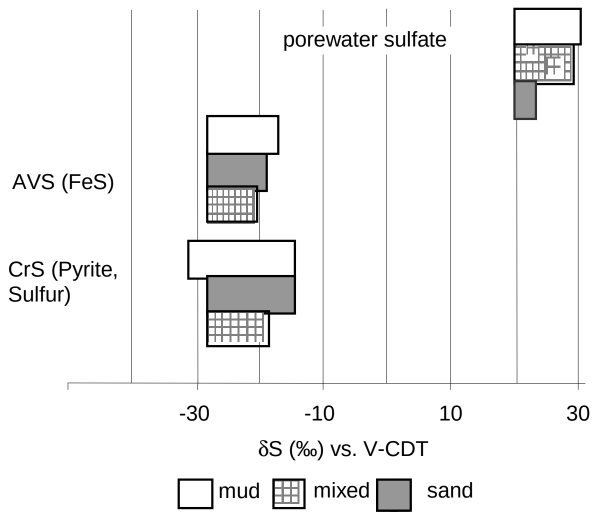

Fig. 8. Stable sulfur isotope discrimination between sulfate and the CRS and AVS fractions.

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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(oxyhydr)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 BOSSELMAN *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.

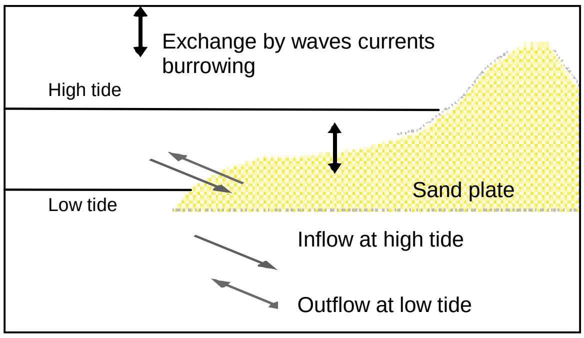

Fig. 1. Sketch of the main advection phenomena on intertidal sand plates.

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 hydrodynamic regime and thus the exchange and conversion rate.

In-situ exchange rates are determined *via* benthic chamber methods. In addition, a more open measuring system is in use where microsensors are deployed to an automatic measuring platform (WALPERSDORF *et al*., this issue) for continuous measurements over periods of days. From microprofiles, measured *in situ*, exchange rates can be calculated. In porous sands both advection and diffusion play a role with variable ratios; this fact has to be taken into account in the interpretation of pore water profiles. Moreover, analyses must be made under steady-state conditions, which are not fully reached in this dynamic environment. We have approached these problems by combining field and laboratory measurements. By a combination of microsensor techniques and benthic chambers we have determined consumption, production and exchange rates of oxygen and compared them with microbial rates of sulfate reduction and methanogenesis.

Furthermore, we have linked the observed phenomena and microbial activities to metal cycling. Iron and manganese profiles were measured in high resolution, both in the solid and the porewater fractions. Gel samplers were used for high-resolution measurements of dissolved species (BOSSELMANN *et al*., this issue). Additionally, metal exchange rates between sediment and surface water were determined using benthic chambers.

A major conclusion from our studies is that despite their rather low organic matter content the permeable sands are much more active than previously assumed. The reason for the high degradation rate is the efficient transport of organics and oxygen into the sand plate by advection. The advection phenomena are heterogeneous in space and time. Fig. 1 schematically shows how and where tides and winds may determine the transport processes.

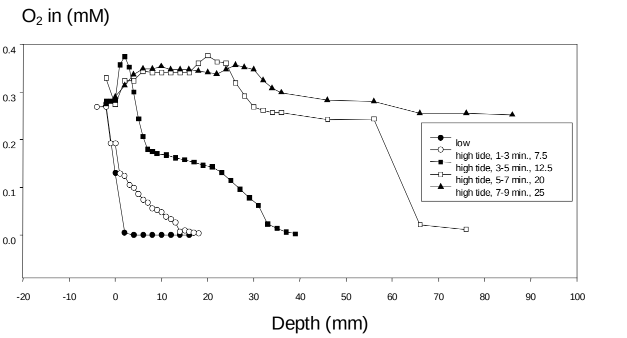

Fig. 2. Transient oxygen profiles measured during a tidal wave in sandy sediments.

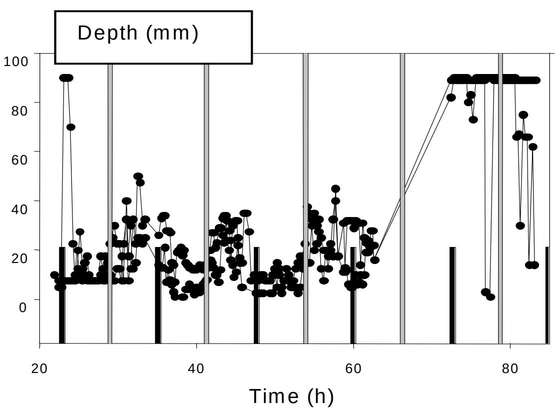

Fig. 3. Penetration depth (in mm) of oxygen measured, over a period of several days with microsensors mounted on a lander. The interruptions of the measurements were caused by broken sensors.

An example of the fast penetration of seawater, saturated with oxygen, during incoming tide into sandy sediments is given in Fig. 2. The profiles were measured at the low-water line, represented by the red arrow in Fig. 1.

An example of long-term experiments in the center of Janssand, where advection to a significant extent is ruled by local hydrodynamics, is presented in Fig 3. Clearly, an effect of tides is also obvious. At the very beginning of the measurement series the microsensors were affected by the presence of worm holes, as can be recognized by deep oxygen penetration. By comparing the oxygen penetration depth with the potential local conversion rates, we could calculate the areal conversion rates on the sand plates (WERNER *et al*, this volume). Almost equally high values were found for spring and summer (Site Königshafen).

When areal sulfate reduction rates from sandy and muddy sites are compared on a seasonal basis (Fig. 4) it becomes clear that temperature controls the activity of sulfate-reducing bacteria in muddy and mixed sediments whereas the availability of organic matter is an additional important factor in permeable sediments. A comparison with areal sulfate reduction rates (close to zero in spring and about 12 $mmol/m^2 day$ in summer) showed that permeable sand plates can be considered as highly active bioreactors where aerobic processes play an important role in the degradation of organic matter. As such the microbial activity in sands is highly relevant for the nutrient cycling in the Wadden Sea ecosystem.

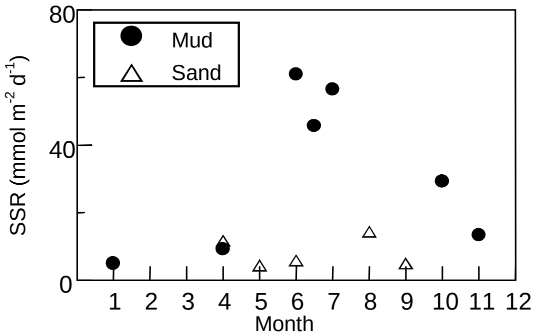

Fig. 4. Seasonal variation of areal microbial sulfate reduction rates in surface sediments. Depth integration for the upper 15 cm.

The complex sulfur and metal cycles are closely linked to each other in intertidal surface sediments (Fig. 5). Oxygen penetration into permeable sediments results in the reoxidation of labile iron(II) sulfides and re-precipitation of reactive iron(oxyhydr)oxides, which are, therefore, enriched in the upper part of the sediment. Acid-volatile sulfur (AVS) is a good indicator for the depth of maximum oxygen penetration caused by wave action or sediment resuspension. Pyrite formation is controlled by the availability of iron and may be slowed by enhanced DOC concentrations.

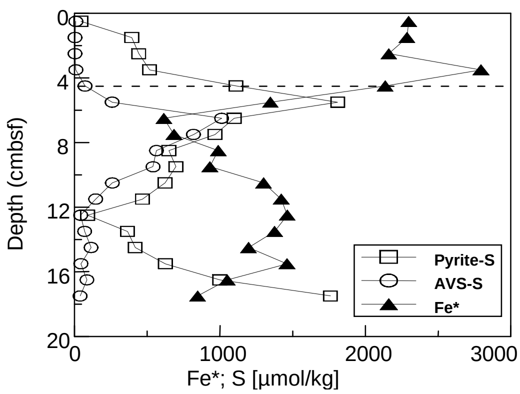

Fig. 5. Downcore variations of sedimentary sulfur species (AVS and pyrite sulfur, and reactive iron (Fe*) at a sandy site in fall. Dashed line marks the supposed maximum oxygen penetration or resuspension depth.

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