



# 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. 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. This 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 base. 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 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.

## Location

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). Sites Neuharlingersiel and Janssand represent intertidal sandy and mixed 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.

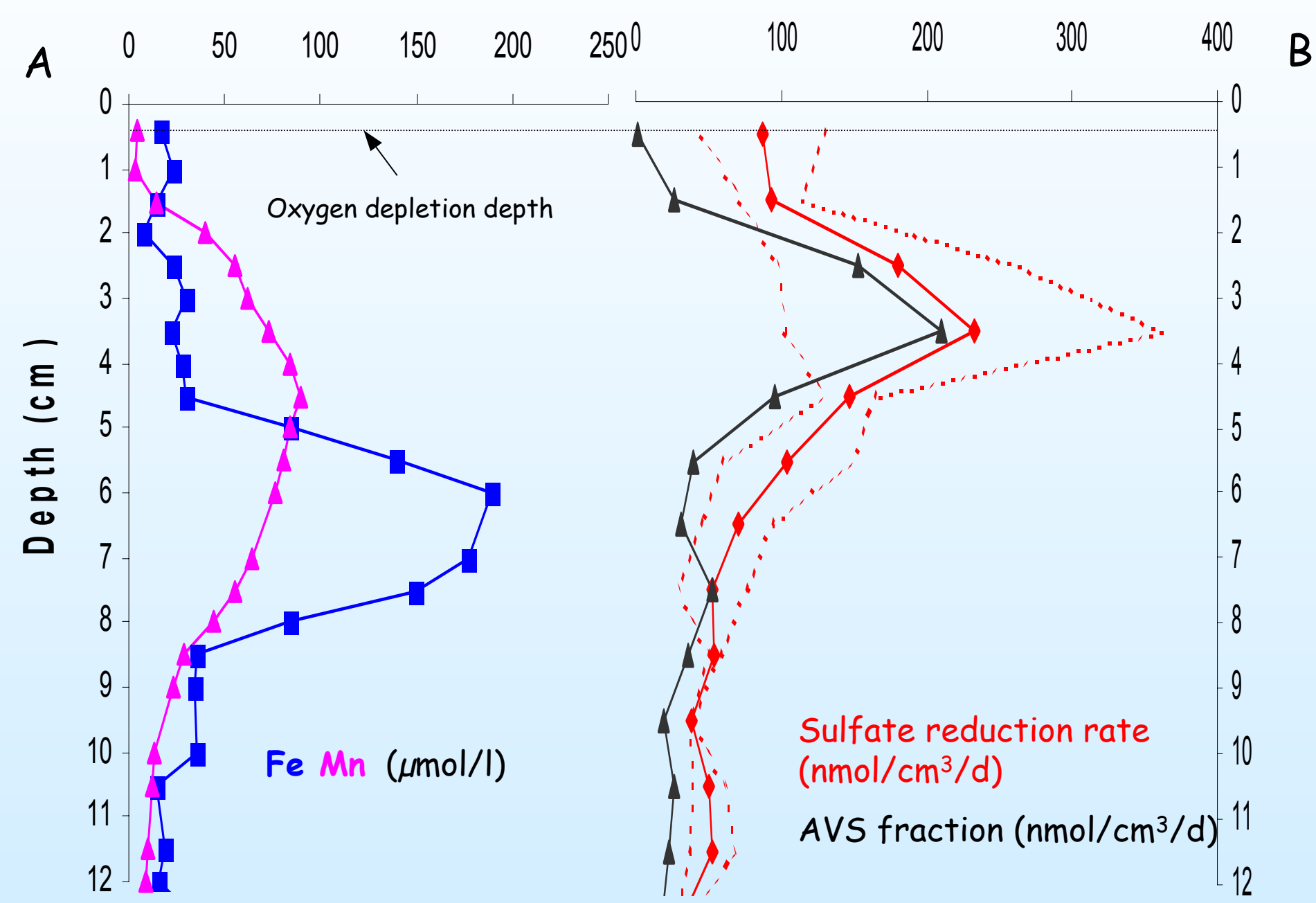


Fig. 2: A Mixed flat at Neuharlingersiel during spring time: Porewater DET profiles of dissolved iron and manganese  
B Range of microbial sulfate reduction rates and the fraction of AVS

## Methods

Sediment cores were analyzed down to 20 cm depth for TOC and water content. Pore waters were analyzed for pH,  $H_2S$ ,  $CO_2$ ,  $NH_4^+$  and salinity and ICP-OES/MS was used to measure  $Mn^{2+}$ ,  $Fe^{2+}$ . Additionally, pore waters were analyzed in high depth resolution using DET and DGT gel samplers and *in situ* microelectrodes attached to autonomous lander systems. Different sulfur fractions were quantified as, acid volatile sulfide (AVS, essentially  $FeS$ ) and chromium reducible sulfur (CRS, mostly pyrite,  $FeS_2$ , with minor elemental sulfur) by a two-step-distillation method and isotopically ( $^{34}S/^{32}S$ ) characterized by means of C-irmMS. Microbial sulfate reduction rates were measured by the  $^{35}SO_4^{2-}$ -tracer injection technique. The hydrogen-sulfide production was visualised by using an *in-situ* 2D-SRR-photoemulsion-monitoring technique. Benthic chambers were used to investigate the dynamics of metals and nutrients.

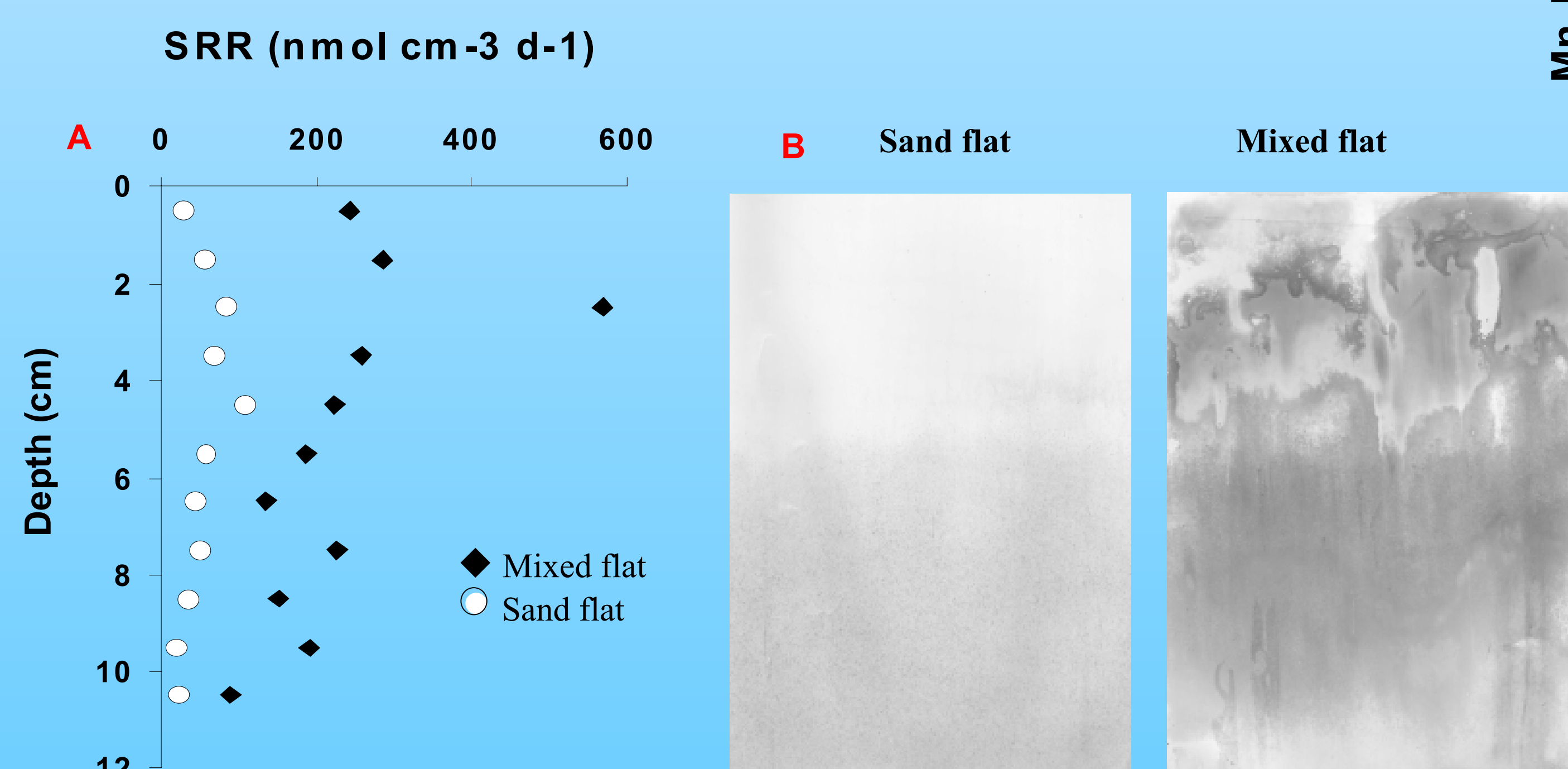


Fig. 5: Sulfate reduction rate in sandy sediments of Janssand and mixed sediment of Neuharlingersiel.  
A Whole core incubation technique with radiotracers.  
B Spatial distribution of SRR monitored by the 2D-photoemulsion-monitoring technique.

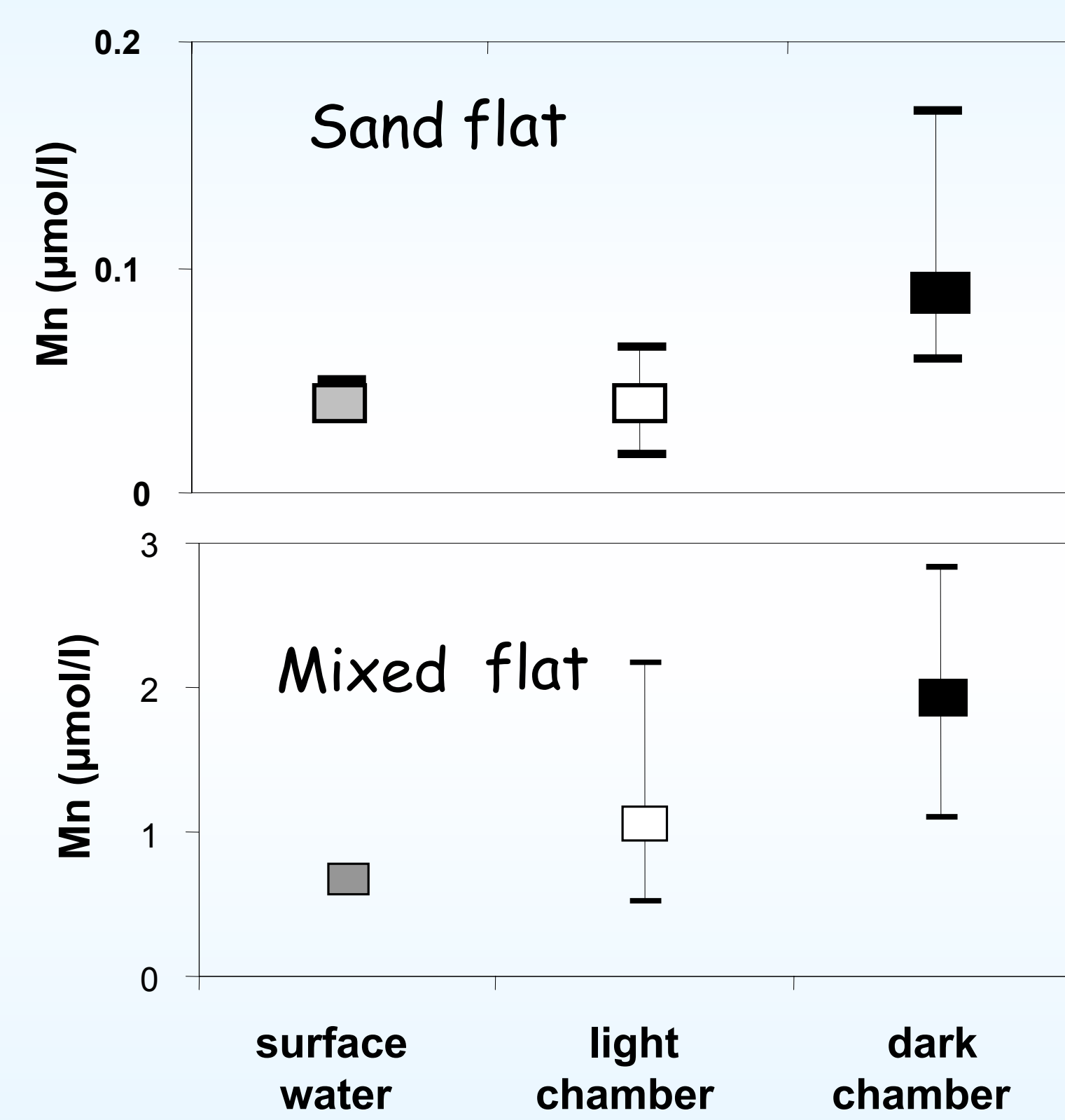
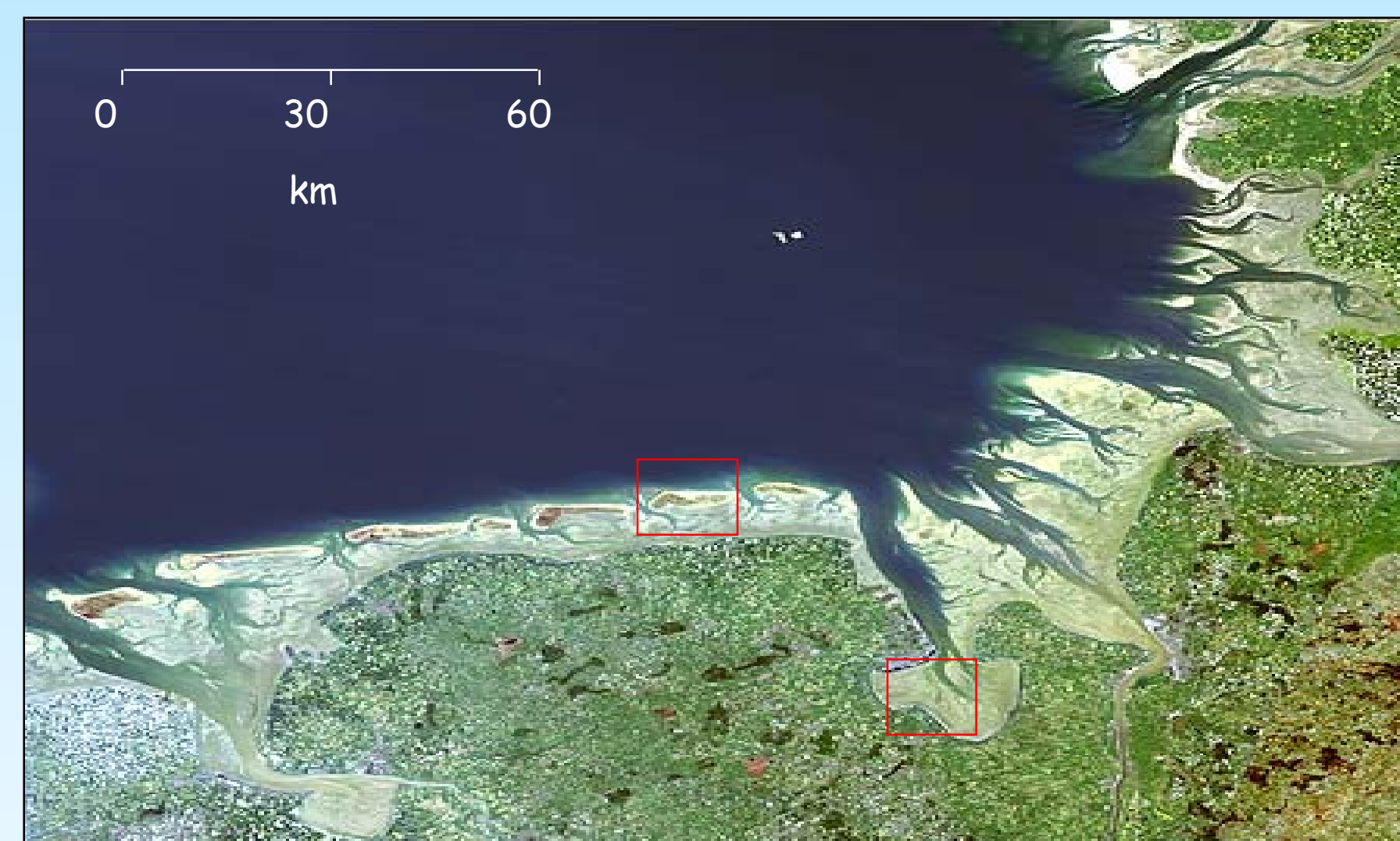


Fig. 3. Average concentration and the total range of liberated dissolved manganese during incubations in summer.

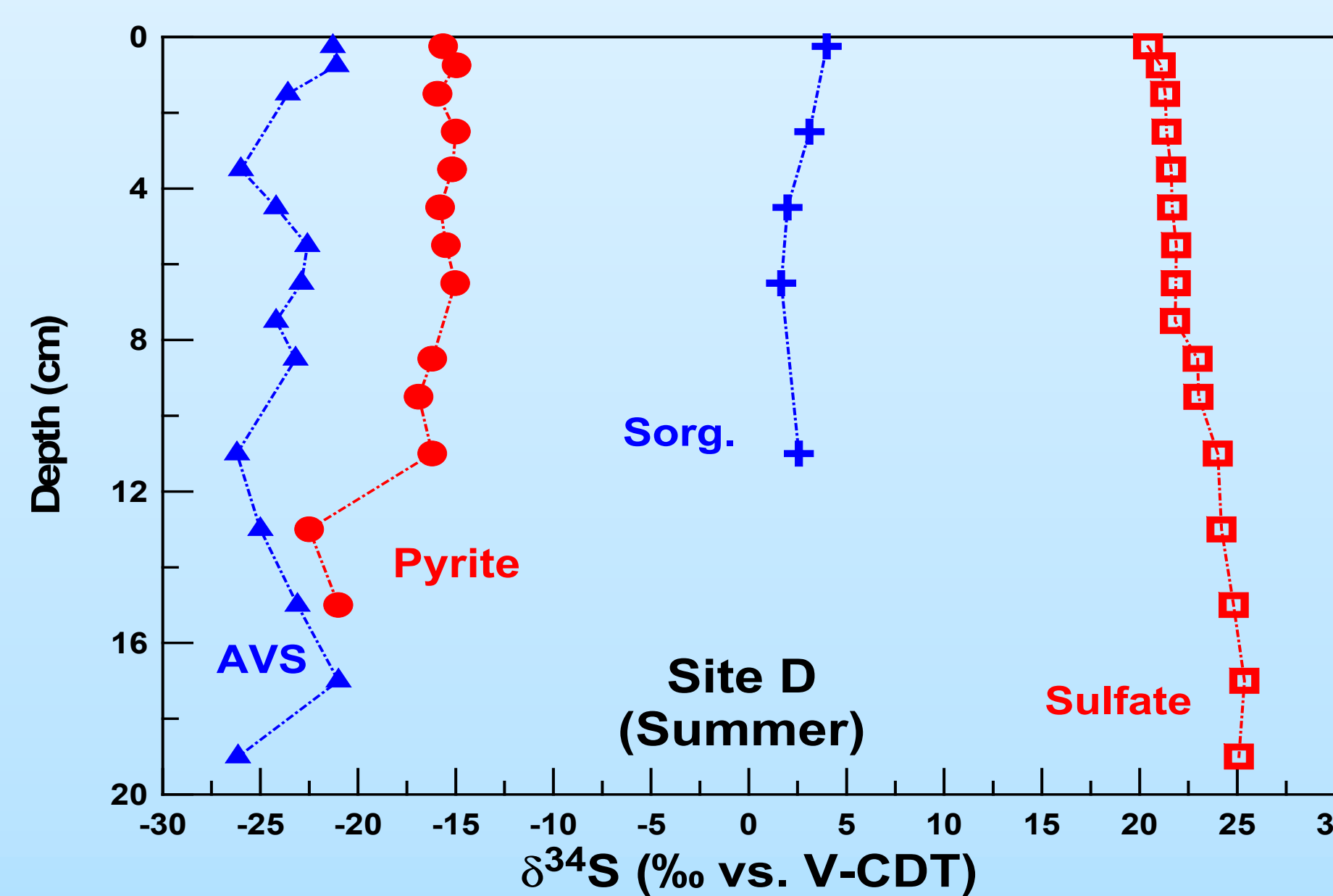


Fig. 5: Downcore variation of isotopic composition sedimentary sulfur species at Dangast (summer)

## 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.

Fig. 2 shows 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. The maximum concentration of dissolved iron below the depletion of sulfate reduction is compatible with the decline of hydrogen sulfide at this depth.

Reduced  $Fe^{2+}$  and  $Mn^{2+}$  diffuse to the sediment surface and are re-oxidized again. Experiments with benthic flux chambers demonstrate that dissolved manganese is able to diffuse out of the sediment. Fig. 3 shows the range of the dissolved manganese concentration measured during short-time (maximum 4 h) incubations with light and dark chambers. At both sites (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.

When areal sulfate reduction rates from sandy and muddy sites are compared on a seasonal base (Fig. 4) it becomes clear that temperature is controlling the activity of sulfate reducing bacteria in muddy (and mixed) sediments while the availability of organic matter is an additional important control in permeable sediments. A similar seasonal response is shown in the manganese retention capacity for the mud flat site (Fig. 4) indicating a coupling with the temperature-dependent microbial activity.

Fig. 5 shows the spatial distribution of the *in situ* hydrogen sulfide production using the 2D-monitoring technique, compared with the sulfate reduction measured with radiotracers. Due to the typically low organic matter contents sulfate reduction rates in the sandy sediments from Janssand were much lower than in the mixed sediment at Neuharlingersiel.

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. 6). Whereas AVS and  $SO_4^{2-}$  mainly reflect bacterial metabolism, the pyrite composition is additionally influenced by physical mixing processes.

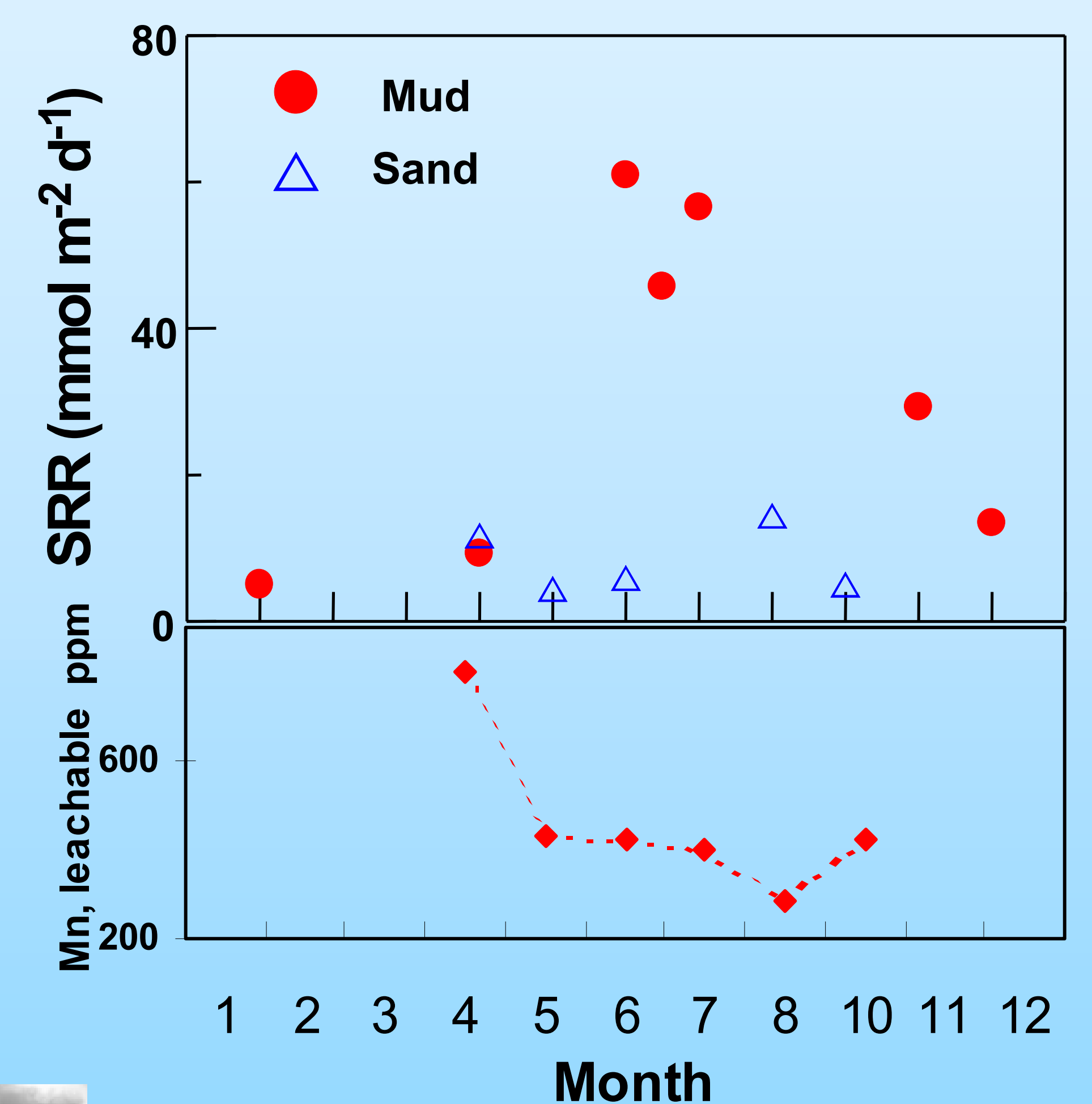


Fig. 4: Seasonal development of depth integrated sulfate reduction rate (nmol/m<sup>2</sup>/d) and leachable, reactive manganese oxides (ppm).

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