



Biogeochemistry of the Sulfur Cycle in Intertidal Surface Sediments of the German Wadden Sea



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Introduction & Outline

In permeable, near-surface sandy sediments the application of ^{35}S -labeled radioactive sulfate yields high activities of sulfate-reducing bacteria (Fig. 1). Highest sulfate reduction rates (SRR) are found in the suboxic zone close to the sediment surface and show, due to the temperature dependence of metabolic processes, a distinct seasonality (Fig. 2). Dissolved sulfate is reduced to H_2S . A minor portion of H_2S further reacts to form iron sulfides [3,4]. Iron-limited conditions may lead to the accumulation of sulfide, but microbial and/or chemical oxidation to sulfate or intermediate sulfur species lead to a burial of gross sulfide produced of down to 10%. Therefore, the biogeochemical sulfur cycle is closely linked to reactions of oxygen, iron, (nitrate) and manganese [1]. The fractionation of S and O isotopes is especially suited to characterize the complex reactions. Results presented are from sandy, mixed and muddy intertidal North Sea coastal areas of Spiekeroog and Sylt Islands, and Westerhever [1] (German North Sea). Sampling sites differ in hydrodynamic regime, and corresponding sediments in grain sizes, organic matter (OM), water, and metal (Fe, Mn) contents.



Research vessel (tjaelk) during winter time at an intertidal sand plate site (Janssand [5])



Black spots, found on permeable sandy sediments, can act as windows for nutrients and reduced substances [2,3,5]

Especially, temperature and OM load were considered as process-controlling variables. Most sediments are characterized by the abundance and highest activity of sulfate reducers (MSR) in the top 15 cm. Depth-integrated sulfate reduction rates in sandy sediments were lower than in the muddy and silty sediments. In OM-rich sediments, temperature controls seasonal changes in MSR. In OM-poor, sandy sediments, MSR is additionally controlled by the abundance of degradable organic matter (OM). Another factor is the transport of solutes across the sediment-water interface (e.g. O_2 , DOC). Pore water sulfate concentrations remain essentially constant within the top 2-3 dm under conditions where sulfide reoxidation takes place and the exchange of sulfate across the sediment-water interface is not limited (not net MSR) (Fig. 5). A local enhancement of sedimentary OM in sands may lead to the near-surface consumption of dissolved sulfate and the accumulation of H_2S [2], often associated with anaerobic oxidation of methane (AOM).

Sulfate and AVS (essentially FeS) reflect in-situ bacterial metabolism and re-oxidation of sulfur compounds, but pyrite compositions are additionally superimposed by transport processes (Fig. 5). Fe-limitation and enhanced DOC concentrations minimize isotope exchange with pyrite [3,4] (Fig. 4). Lowered in-situ isotope discrimination in sandy sediments locally loaded with enhanced OM indicate enhanced cellular SRR (Fig. 3, 4).

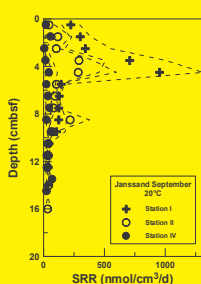


Fig.1: Microbial SRR on a transect from top (stn. IV) to boundary of a sandy plate (stn. I) (Janssand, autumn)

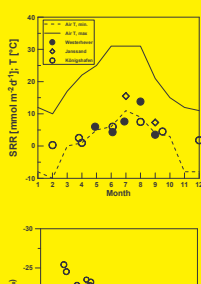


Fig.2: Sampling sites differ in grain sizes, organic matter (OM) and metal (Fe, Mn) contents. Seasonal variations of depth-integrated SRR (15cm) for different intertidal sands [1] compared to air temperature. SRR in mixed and muddy sediments show the same trend at higher rates.

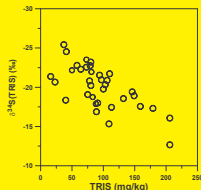


Fig.3: Variations of content and S isotopic composition of TRIS: Enhanced isotope discrimination coupled to lower SRR (sand flat; Westerhever [1])

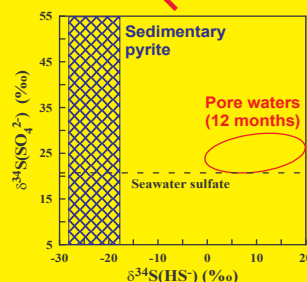
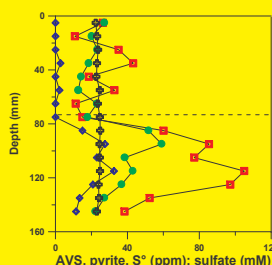


Fig.4: Loading experiment with enhanced OM (starch) in a permeable sand flat (Gröninger Plate, Spiekeroog). No sulfur isotope exchange occurs between pyrite and H_2S within 12 months (after [4]) due to high DOC concentrations. Due to MSR, ^{32}S is co-enriched with ^{34}S in residual sulfate.



2D-Photopaper monitoring of MSR in intertidal surface sediments



Sandwatt Sylt
 - Acid volatile sulfides (FeS)
 - Pyrite (FeS₂)
 - Elemental Sulfur (S²⁻)
 - Sulfate

Fig.5 Depth variations of contents and sulfur isotopic compositions of dissolved and solid sulfur species (Hausstrand-Sylt, May). Dashed line: Maximum O_2 penetration depth. Intense sulfide oxidation takes place in the top parts of the sediments linking the sulfur cycle partly to the dynamics in dissolved and solid phase Mn and Fe, as for instance AVS and Fe(III) distributions.

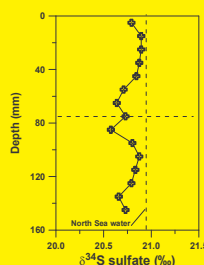


Fig.6: SRR and pore water metal concentrations (gel sampler) in the suboxic zone of a silty mixed flat sediment (no sulfide accumulation in the upper 12 cmbsf)

References

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Acknowledgements:

The study is supported by Deutsche Forschungsgemeinschaft during DFG research group 'Biogeochemistry of the Wadden sea' Grant JO307/4-1, -2, BMBF, Berlin, and MPG, Munich. MEB wishes to thank J. Rullkötter for the possibility to use the gas mass spectrometer at the ICBM Oldenburg