Geophysical Research Abstracts, Vol. 8, 09919, 2006
SRef-ID: 1607-7962/gra/EGU06-A-09919

Pore water gradients below oxidized and reduced surfaces of intertidal surface sediments

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Introduction: Organic matter is mineralized in marine sediments by microbial activity using predominantly oxygen, sulfate, and Fe(III) and Mn(IV) (oxyhydr)oxides as electron acceptors. In intertidal surface sediments, the development of steep compositional and physico-chemical gradients is a common phenomenon. Typically oxygen is consumed rapidly within the upper few mm of marine sediments. In permeable sediments, however, oxygenated bottom waters may flow through the upper part of the surface sediments leading to enhanced participation of oxygen in element cycling. Additionally, black anoxic surface sediments, so-called 'black spots', are locally formed, indicating a disturbance in the balance of the biogeochemical processes, and may act as windows for the liberation of reduced substances into the bottom water or the atmosphere. In the present study, the pore water composition below oxic and anoxic surfaces of intertidal sandy sediments is investigated using a number of different techniques in the frame of the DFG-research group 'BioGeoChemistry of the Wadden Sea'. Methods: Pore waters have been sampled down to 40 cmbsf using pore water lances, diffusion samplers, centrifugation of sediment core sections, and lander-based microsensors. Water samples are analyzed, salinity, dissolved O2, pH, SO42-, H2S, Cl-, Fe2+, Mn2+, TA, PO43-, NO3-, NH4+, H4SiO4 , Ca2+, and microbial sulfate reduction rates have been analyzed using intact sediment cores. Analytical methods include radio tracer incubation (whole core incubation method), ion chromatography, ion-selective electrodes, spectral photometry, titration method, and isotope-ratio monitoring mass spectrometry. Results and discussion: Sulfur sediment are characterized by high sulfur reduction rates exhibiting maxima between about 5-10 cm. Rates

are higher below anoxic sediment surfaces (Ćblack spots‘), associated with decreased oxygen penetration depths, and proton activities. Anaerobic metabolic activity in pore waters below Black Spots leads to significantly enhanced concentrations of sulfide, ammonium, DIC, phosphate, silica (steep gradients), and a net consumption of sulfate. Enrichments in DOC and methane has been observed. They act as windows for reduced substances to surface waters (and the atmosphere).