



Sulfur and carbon isotope biogeochemistry of a rewetted brackish fen

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Coastal wetlands are at the interface between terrestrial freshwater and marine and exhibit very specific biogeochemical conditions. Intermittent sea water intrusion affects metabolic pathways, i. e. anaerobic carbon metabolism is progressively dominated by sulfate reduction with lower contribution of methanogenesis whilst methane production is increasingly shifted from acetoclastic to hydrogenotrophic. Due to expanding anthropogenic impact a large proportion of coastal ecosystems is degraded with severe implications for the biogeochemical processes.

We use concentration patterns and stable isotope signatures of water, sulfate, dissolved carbonate, and methane ($\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$) to investigate the S and C metabolic cycle in a rewetted fen close to the southern Baltic Sea border. Such studies are crucial to better predict dynamic ecosystem feedback to global change like organic matter (OM) decomposition or greenhouse gas emissions. Yet, little is known about the metabolic pathways in such environments. The study site is part of the TERENO Observatory „Northeastern German Lowlands“ and measurements of methane emissions have run since 2009. High methane fluxes up to $800 \text{ mg m}^{-2} \text{ hr}^{-1}$ indicate that methanogenesis is the dominant C metabolism pathway despite of high sulfate concentrations (up to 37 mM). The presented data are part of a comprehensive biogeochemical investigation that we conducted in autumn 2014 and that comprises 4 pore water profiles and sediment samples within a transect of 300-1500 m distance to the Baltic Sea.

Depth of organic layers ranged from 25 to 140 cm with high OM contents (up to 90 dwt.%). Sulfate/chloride ratios in the pore waters were lower than in the Baltic Sea for most sites and sediment depths indicated a substantial net sulfate loss. Sulfide concentrations were negligible at the top and increased parallel to the sulfate concentrations with depth to values of up to 0.3 mM. One pore water profiles situated 1150 m from the Baltic Sea coast line exhibited a significant excess of sulfate. Preliminary sulfur isotope analysis of pore water sulfate from a location nearest to this profile revealed an enrichment in ^{34}S (24.9 to 41.8‰) in comparison to Baltic Sea sulfate (21‰). This confirms high degrees of net sulfate reduction. Considering the yet high sulfate concentrations we hypothesize that local processes might supply additional sulfate and that the sulfide produced from sulfate reduction might either be lost by upwards diffusion towards the atmosphere or converted into other S compounds such as pyrite or organic compounds. The isotopic signatures of methane ($\delta^{13}\text{C}$: -68 to -57‰ and $\delta^2\text{H}$: -133 to -157‰ respectively) indicated acetoclastic methanogenesis to be the most dominant methane production pathway. However, estimated fractionation factors are comparatively high (1.050-1.065). Enrichment of heavy ^{13}C in methane at the top of the sediment was either caused by methane oxidation or variation in substrate availability (e. g. due to peat degradation).

The interpretation of our data in the light of further results will provide deeper insights into metabolic pathways and possible interactions between both coupled element cycles for coastal ecosystems.