

## Carbon, manganese, iron, and sulfur cycling in oligohaline sediments

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Microbial sulfate reduction is a key process in modern marine sediments as a major contributor to the oxidation of detrital organic carbon and methane. Transformations of the resulting sulfide are coupled to, and strongly influence, the cycling of manganese, iron and other elements. A less prominent role is generally assumed for sulfur cycling in freshwater sediments and, by analogy, in sediments of the Precambrian ocean, where sulfate levels were comparable to modern freshwater systems. However, our understanding of how sulfur cycling and its wider biogeochemical effects vary as a function of sulfate level is limited. We experimentally investigated the contributions of sulfate reduction to organic carbon and methane oxidation, and the associated isotope systematics in sediments of the Bothnian Bay, an oligotrophic and oligohaline basin with manganese- and iron-rich sediments.

Despite sulfate concentrations of only 2–3 mM and up to 2 and 4 wt% reactive manganese and iron, respectively, sulfate reduction accounted for 55–80% of anaerobic carbon oxidation, while dissimilatory manganese and iron reduction accounted for most of the remainder. Hydrogen sulfide was not detectable in the porewater, but comparison of <sup>35</sup>SO<sub>4</sub><sup>2-</sup>-based sulfate reduction rates and diffusive fluxes suggested ≤50% internal reoxidation of sulfide to sulfate despite high reactive iron levels. A low degree of reoxidation was further supported by a shallow slope of  $\delta^{18}\text{O}_{\text{sulfate}}$  vs.  $\delta^{34}\text{S}_{\text{sulfate}}$  of ~0.3. Sulfate was also indicated as the main oxidant for methane as more than 85% of the diffusive methane flux was consumed in the sulfate-methane transition zone (SMTZ) located at 10–40 cm depth, depending on the station. Above the SMTZ, sulfate reduction was associated with an apparent sulfur isotope effect of ~55‰, whereas fractionation decreased in the SMTZ, suggesting a much smaller effect for sulfate-dependent methane oxidation.

In summary, the sulfur cycle impacts biogeochemistry in Bothnian Bay sediments substantially despite low sulfate concentrations. Contributions from dissimilatory manganese and iron reduction are limited by the near absence of bioturbation, and the reactivity of iron oxides in the sulfate reduction zone appears too low to support substantial oxidation of either sulfide or methane, while anaerobic methane oxidation proceeds at micromolar sulfate levels.