



Biogeochemistry of sulfur in Gdansk Bay sediments (Baltic Sea)

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In marine sediments, the biogeochemistry of sulfur cycling is fundamentally important to the anaerobic oxidation of organic matter. Sulfide produced from sulfate reduction may be trapped and buried as organic sulfur and pyrite. Organic sulfur and its isotopic composition are of specific interest due to the impact of sulfate reduction on organic carbon preservation and the potential link of compound specific sulfur isotopes to specific microbial processes (Werne et al., 2001, 2008). Gdansk Bay (Poland) provides a natural laboratory to study how a) low salinity (9-11), b) high organic matter deposition (5- 6%), and c) high sedimentation rates (4 -7mm a⁻¹) (Kunzendorf et al., 1998) in the shallow water (50 – 100 m depth) of the Baltic Sea impact sulfur and carbon cycling. During a recent research expedition with the R/V Oceania to Gdansk Bay in November, 2009, four stations were sampled using a small gravity corer. The samples were collected to determine dissolved methane, sulfate, and sulfide. Solid phase measurements include total inorganic and organic carbon (TOC), total sulfur (TS), acid volatile sulfur (AVS), chromium reducible sulfur (CRS), organic sulfur (OS) as well as their isotope compositions. Additionally, radio-tracer experiments for sulfate reduction rates were performed. Finally, the $\delta^{34}\text{S}$ values of OS were calculated based on an isotope mass balance model. The depth-integrated sulfate reduction rates varied from 180 to 4000 nmol/cm²/day¹ resulting in different sulfate and methane gradients. Sedimentary sulfur was observed to be present as CRS (24 to 424 $\mu\text{mol g}^{-1}$), AVS (0 to 166 $\mu\text{mol g}^{-1}$) and organic sulfur (25 to 400 $\mu\text{mol g}^{-1}$). CRS and OS increased while AVS decreased with depth. OS/ TOC ratios varied between 0.01 and 0.2, (most of values >0.04). The light $\delta^{34}\text{S}$ value of AVS (-22.4 to -5.0‰, CRS (-46.5 to 1.1‰ and total S (-44.5 to -0.9‰ were indicative of bacterial sulfate reduction. $\delta^{34}\text{S}$ of the OS was calculated by an isotope mass balance model and resulted in values of -44.2 to 10.0‰ which suggested that sulfurization of organic matter takes place via inorganic reduced sulfur. The sulfurization of the organic matter may enhance preservation of organic carbon in the Gdansk Bay sediments.

[1] – Werne, J.P., Lyons, T.W., Hollander, D.J., Formolo, M.J., Sinninghe Damste, J.D., 2001. Reduced sulfur in euxinic sediments of the Cariaco Basin: sulfur isotope constraints on organic sulfur formation. *Chem Geol* 195, 159 – 179.

[2] - Werne, J.P., Lyons, T.W., Hollander, D.J., Schouten S., Hopmans, L.C Sinninghe Damste, J.D., 2008. Investigating pathways of diagenetic organic matter sulfurization using compound – specific sulfur isotope analysis. *Geo-chim. Cosmochim. Acta* 72, 3489 – 3502.

[3] - Kunzendorf, H., Emeis, K.C., Christiansen, C., 1998. Sedimentation in the Central Baltic Sea as viewed by non destructive ²¹⁰Pb dating. *Geografisk Tidsskrift*. Bind 98.