

## Effects of biogenic substances on the light-induced redox cycling of iron in surface waters

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### Chemical Characterisation of Biogenic Substances

Dissolved biogenic substances occurring in surface waters are complex mixtures of high- and low-molecular weight dissolved organic matter (HMW DOM and LMW DOM, respectively), and of hydrophilic and hydrophobic substances. We have characterised DOM fractions gained by ultrafiltration (1 kD) and C18 solid phase extraction of water samples taken from the River Tagliamento, Italy, by using spectroscopic methods including multidimensional solution-state NMR (Kaiser et al., submitted).

### Effect of DOM Fractionation on the Light-Induced Redox Cycling of Iron

Irradiation of HMW and LMW DOM (from water samples longitudinally and seasonally collected from the River Tagliamento) with simulated sunlight resulted in the formation of Fe(II). Iron(II) steady-state concentrations (normalised to DOC concentration) were significantly higher in irradiated HMW DOM fractions than in irradiated LMW DOM fractions. This phenomenon may be explained by either Fe(II) being more efficiently formed in the presence of HMW substances and/or Fe(II) oxidation occurring faster in the presence of LMW substances.

### Effect of DOM Origin on the Light-Induced Redox Cycling of Iron

Irradiation of unfiltered water samples from two Swiss lakes, Melchsee and Greifensee, with simulated sunlight revealed considerably faster kinetics of both Fe(II) formation and Fe(II) disappearance (after the light-source was turned off) in Melchsee than in Greifensee water, although Fe(II) steady-state concentrations were similar. Mathematical kinetic modelling and comparison with these experimental results suggest that superoxide is a key intermediate in the light-induced redox cycling of iron in these two lakes, and that superoxide steady-state concentrations are considerably higher in Melchsee than in Greifensee (Emmenegger et al., 2001). DOM present in the oligotrophic Melchsee is largely terrestrial-derived, whereas in the eutrophic Greifensee it is algal-derived.

### References

- Emmenegger L., Schönenberger R., Sigg L. and Sulzberger B., (2001). *Limnol. Oceanogr.* **46**, 49-61.  
Kaiser E., Simpson A.J., Dria K.J., Sulzberger B. and Hatcher P.G., *Environ. Sci. Technol.*, submitted.

## Sulfate reduction rates in deeply buried marine sediments

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Bacterial sulfate reduction rates (SRR) in samples from three sites from the Nankai Trough, an accretionary wedge off Japan (ODP Leg 190), were directly assessed by injecting radiolabeled <sup>35</sup>SO<sub>4</sub> and measuring its turnover to reduced sulfur. At Sites 1173 and 1174 sulfate was depleted within the first few meters below the sea floor and reappeared at 200 m and 600 m respectively. SRR, however, were only measurable in the surface sediments. In contrast, Site 1177 exhibited significant sulfate turnover at depths of 500 to 700 m (up to 400 pmol/cm<sup>3</sup>/d). These depths comprise a turbidite sequence containing both high organic carbon content and near seawater concentrations of sulfate. These results are surprising in light of the age (10 - 15 Ma), and terrestrial provenance of the organic facies. For comparison we will also present sulfate reduction rates on samples just obtained from the Peruvian Continental Margin (ODP Leg 201) - sediments dominated by high marine productivity.