

## Biogeochemical cycling of C, O, and S in an iron rich hypersaline microbial mat

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**Introduction:** Although there are examples of iron rich stromatolites in the geological record, possible modern analogues have not been studied in detail as yet. We chose a cyanobacterial mat from a Solar Saltern on the Rhone Delta (Southern France) as a model system to quantify the major biogeochemical processes and to study sulfide oxidation in particular.

**Approach:** During a diel cycle microsensor profiles of O<sub>2</sub>, H<sub>2</sub>S, and pH were repeatedly measured *in situ* in the top few millimeters of the mat. At the same time the sulfate reduction rate (SRR) was determined with <sup>35</sup>S-radiotracer and mapped in 2D with <sup>35</sup>SO<sub>4</sub><sup>2-</sup>-coated silver foils. Samples for high-resolution chemical speciation (Fe(II), Fe(III), Mn(II), S<sup>0</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>) were also taken. Enrichments for several sulfur- and iron-metabolizing microorganisms were established to complement the geochemical data.

**Results:** Microsensor profiles revealed that, unlike in other mat types, sulfide is absent in the top few millimeters even during most part of the night. However, very high SRR of up to 1800 nmol cm<sup>-3</sup> h<sup>-1</sup> were determined by the <sup>35</sup>SO<sub>4</sub><sup>2-</sup>-radiotracer method. The rates were about 6 times higher during the day than the night and closely followed the diel temperature oscillations. The SRR modeled from sulfide microprofiles showed the same trend but were always much lower. During the day the difference between the gross SRR (<sup>35</sup>SO<sub>4</sub><sup>2-</sup>) and net SRR (modeled) can be explained by chemical and biological oxidation of sulfide in the oxic zone and by anoxygenic phototrophic sulfide oxidation below. These processes do not operate in the dark, but measurements of Fe(II), Fe(III), and S<sup>0</sup> suggest that an iron-oxide pool is built up during the day and serves as the oxidant for sulfide in the night. As a consequence, the sulfide concentrations in the top millimeters of the mat are kept low, and the SRR calculated from profiles is strongly underestimated. In the uppermost layer, S<sup>0</sup> and possibly FeCO<sub>3</sub> are produced during the reaction of sulfide with iron oxides. FeS is formed deeper down and reaches concentrations as high as 200 μmol cm<sup>-3</sup>.

**Conclusion:** Exceptionally high iron concentrations were measured in a hypersaline microbial mat. The iron oxides in the uppermost layer of the mat act as a rechargeable sulfide buffer and as a result, sulfide oxidation gets temporally decoupled from oxygen production.

## Stable Isotope analysis of volatile organic contaminants at trace levels

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### Background

Compound-specific isotope analysis (CSIA) is a very promising approach to help determining both *in-situ* transformation processes of pollutants in contaminated aquifers as well as sources of groundwater contaminants. Various laboratory studies have demonstrated the potential of this tool in contaminant hydrology (1-3). To date, the use of CSIA in field studies is, however, confined to near source zones of groundwater contamination with high pollutant concentrations. The method detection limits in CSIA are in the order of 150 ppb for chlorinated solvents using solid phase microextraction as preconcentration method (4). Hence the method sensitivity is currently too low for applications of CSIA to investigate tail and fringe zones of contaminant plumes, which would be most helpful to assess natural attenuation processes in the field.

### Improvement of Sensitivity and Field Application

In order to improve the method detection limits of CSIA, we used online purge and trap (P&T) preconcentration and investigated its effects on the isotopic composition of the analytes. Evaluated parameters include purge time, desorption temperature and trap material. Isotopic fractionation effects of the various processes involved in P&T (i.e., evaporation, sorption, desorption, and condensation of the analytes) have been evaluated for a series of analytes. The effects were found to be compound-specific but showed a high reproducibility. The developed P&T-GC/IRMS method allows reproducible δ<sup>13</sup>C-determinations for volatile organic compounds at concentrations below 5 μg/L. P&T-GC/IRMS was successfully applied to study the fate of halogenated solvents in a contaminant plume downgradient of a municipal landfill. Contrary to previous evaluations based on concentration data alone, our P&T-GC/IRMS data strongly suggest the absence of *in-situ* degradation of trichloroethene (TCE) despite the presence of *cis*-dichloroethene, a known metabolite of (TCE).

### References

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