# Biogeochemical processes in the stratified water column of Mariager Fjord (Denmark)

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Mariager Fjord is a narrow, shallow fjord in north-eastern Denmark connected to the Kattegat by a long (>20 km) channel of less than 10 m depth that limits water exchange between the sea and the central basin (28 m depth). The water column in the central basin is stabilized by a density gradient and exhibit a distinct redox stratification, where the $O_2$ downward flux balances the overall upward $H_2S$ flux (Ramsing *et al.*, 1996; Fenchel *et al.*, 1995).

In order to better understand the redox reactions taking place in the chemocline and the microorganisms involved, high resolution profiles of different electron donors ($Fe^{2+}$, $Mn^{2+}$, $NH^{4+}$, $H_2S$), acceptors ($Fe^{3+}$, $Mn^{4+}$, $NO_3^-$, $O_2$) and sulphur intermediates were determined and combined with direct rate measurements ($^{35}$S-sulphate-reduction in the sediment, $^{14}$C-bicarbonate fixation rates in the water column). Additionally, traditional microbiological methods, e.g. enrichments and MPN counts, as well as modern molecular methods were applied.

## Results

The chemocline was located between 13.25 and 13.5 m, and varied slightly from day to day. The gradients of oxygen and sulphide were very steep and showed only little overlap (15-50 cm). Below the chemocline sulphide increased monotonically with depth. In contrast to an earlier study, no clear evidence was found for anaerobic sulphide oxidation as concluded from the $H_2S$ profiles (Ramsing *et al.*, 1996). In addition to sulphide and sulphate, elemental sulphur, thiosulphate and sulphite were determined. Whereas sulphite was not detected, a peak of thiosulphate (5.7 μM) was found just below the zone of $O_2/H_2S$ coexistence. Below 15 m thiosulphate concentrations decreased to a background level of about 100 nM. Elemental sulphur was found from 12.75 m to 14.25 m with a maximum concentration of 19 μM in the chemocline. Below 14.25 m the elemental sulphur concentration was below the detection limit of 1 μM.

Peaks of particulate manganese (3.5 μM) and particulate iron (3.3 μM) were found above the chemocline, whereby the manganese maximum was located above the iron maximum. Below these maxima dissolved reduced manganese and reduced iron increased and reached concentrations of 25.6 μM and 1.2 μM respectively. Ammonia concentrations decreased from 240 μM at the bottom to 37 μM in the chemocline. In the oxic layer ammonia decreased further to 3 μM.

## Discussion

Although anoxygenic phototrophs were enriched from the chemocline and below, they do not seem to contribute significantly to sulphide oxidation as was concluded from the shape of the sulphide profile. That no pigments of phototrophic sulphide oxidizers and no associated elemental sulphur was found at these depth support this conclusion. Dark incubation experiments with $^{14}$C-bicarbonate showed a maximum of carbon fixation ( 2.3 μmol $l^{-1}$ $h^{-1}$) just below the chemocline, indicating a significant population of chemolithoautotrophs. The responsible organisms for this peak in $CO_2$-assimilation remain to be identified. Besides thiosulphate (2 μM) and very low levels of nitrate (0.4 μM), apparently no electron acceptors are present below the chemocline. This region could therefore form a niche for anaerobic nitrate reducing sulphide-oxidizers or thiosulphate-disproportionating bacteria.

Since elemental sulphur and thiosulphate are the main products of the reaction of sulphide with manganese and iron in seawater (Yao and Millero, 1996), our findings may lead to the conclusion that sulphide is to a significant extent oxidized by settling manganese- and iron-oxides. The build-up of intermediate oxidized sulphur pools might be of great importance for the microbial community in the chemocline. Since these compounds are much more stable under oxic conditions and less reactive towards manganese and iron, microorganisms could successfully compete for these intermediates as energy source or electron acceptors.

## References

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