Systematics and energetics of volatile fatty acids in Baltic Sea sediments

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Volatile fatty acids (VFAs) play a key role as intermediates in the subsurface microbial mineralization of organic matter (OM). VFAs are generated by fermentation and hydrolysis and at the same time represent substrates for the terminal processes of OM mineralization, e.g. sulfate reduction (SR) and methanogenesis (MG). Because the VFA generation is the rate determining step in the overall mineralization process, pore water VFA concentrations are usually at low levels and represent a steady-state of generation and consumption. The steady-state concentration is linked to physiological and thermodynamic constraints and the value influence the energetic yield of both production and consumption of the acids.

We applied a newly developed 2D IC-MS method [1], and show for the first time the tightly balanced VFA concentrations in a sequence of sulfate-reducing and methanogenic sediments from the Baltic Sea recovered during IODP Exp. 347 and subsequent cruises. Acetate, Propionate and Butyrate increased by a factor of ~10 within approx. 100 m of sediment whereas formate remained in the range of 0.5 to 10 µM with the majority of samples at ~5 µM. Acetate increase from ~5 µM in surface-near sediments to up to 50 µM in the depth, typical concentrations in the sulfate zone were 3 to 10 µM whereas in the methane zone concentrations were mostly between 10 and 30 µM. Propionate and butyrate increased similar to acetate but concentrations were approx. one and two orders of magnitude lower, respectively. Sharp peaks in concentrations might reflect non steady-state situations, e.g. at lithological interfaces. Calculation of Gibbs energies of acetate utilizing SR and MG showed that there is a significant energy yield from both of these pathways in both, the sulfate and the methane zone. The lowest energy yield from SR was observed at the sulfate-methane transition zone approaching -20 kJ (mol acetate)$^{-1}$. Lowest energy yields from MG were observed in methane saturated sediments at values ~ -10 kJ (mol acetate)$^{-1}$. These lowest energy yields are similar to previous observations for H_2-driven SR and MG [2], but fail to explain the separation of SR and MG zones.

[1] Glombitza et al., 2014. *L. & O.:Methods.*12, 455-468.
[2] Hoehler et al., 2001. *FEMS Microbiol. Ecol.* 38, 33-41.