

Volatile Fatty Acids, key intermediates for microbial metabolism in subsurface sediments – generation and fate

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Volatile fatty acids (VFAs) are key intermediates in the subsurface microbial metabolism. They are generated by fermentation or by abiotic hydrolysis from sedimentary organic matter (OM) and represent important substrates for the terminal processes of anaerobic OM mineralization. Usually VFAs are generated and consumed in the same sediment horizon. By using a newly developed analytical approach employing 2D IC-MS [1], we have found that VFA pore water concentrations are closely balanced at low concentrations as the result of a rapid turnover by the anaerobic microorganisms. Typical acetate pore water concentrations are $\sim 5 \mu\text{M}$ for sulfate reducing sediments (e.g. Greenland shelf, [2]) and $\sim 15\text{-}20 \mu\text{M}$ for methanogenic sediments (e.g. Baltic Sea, IODP Exp. 347, *unpubl.*). Turnover times of the pore water acetate pool increase strongly with depth, from a few hours to a few years. In deep sediments, the ongoing maturation of macromolecular OM (i.e. the kerogen) provides significant amounts of VFAs by the release of ester-bound moieties [3]. Thus, OM rich lithologies, e.g. the deeply buried coal beds off Shimokita (IODP Exp. 337) [4] provide a subsurface source of VFAs (*unpubl.*). Because pore water VFAs are usually kept at low concentrations by the microbial consumers, the reactivity of the macromolecular OM controls microbial activity in the subsurface. At geological interfaces, or when microbial respiration is limited by other factors, e.g. increased temperature or the availability of electron acceptors, VFA concentrations can be elevated, suggesting that the tight coupling of production and consumption is out of balance. We will highlight the importance of VFAs as key intermediates for subsurface microbial life, using both published and new unpublished results.

[1] Glombitza et al. (2014) *Limnol. Oceanogr.:Methods* 12, 455. [2] Glombitza et al. (2015) *Front. Microbiol.* 6:856. [3] Glombitza et al. (2009) *Org. Geochem.* 40, 175. [4] Inagaki et al. (2015) *Science* 349, 420.