



Carbon isotopic compositions of volatile fatty acids in sediment/pore-water systems measured by isotope-ratio-monitoring liquid chromatography/mass spectrometry

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In recent decades, our understanding of biogeochemical processes has benefited enormously from the information encoded in the stable carbon isotopic composition of organic molecules. For low-molecular-weight metabolites, $\delta^{13}\text{C}$ values are routinely acquired for methane and used to examine details of its production and consumption. On the other hand, systematic information about the isotopic compositions of volatile fatty acids (VFAs) and other water-soluble metabolites in natural environments is very rare. The isotopic composition of acetate, a ubiquitous intermediate in anaerobic metabolism, is affected by biological processes that produce and/or consume it (Blair et al., 1992; Gelwicks et al., 1989; 1994). Therefore, $\delta^{13}\text{C}$ values of acetate extracted from natural systems are potentially powerful probes to decipher the dominant carbon-transforming processes in situ.

The lack of information about carbon isotopic variations of VFAs in natural environments is due to a lack of methods suitable for their analysis at typical natural concentrations (i.e., μmolar in sediment pore-waters). We have developed a new analytical protocol for sensitive and accurate carbon isotopic analysis of VFAs by isotope-ratio-monitoring liquid chromatography/mass spectrometry (irm-LC/MS). This technique is based on the new FinniganTM LC IsoLink interface that couples an HPLC to commonly used irm-MS-systems (Krummen et al., 2004). Our technique extends the previously accessible concentration range to lower concentrations and minimizes the required sample volume to 0.5-3 mL. The fully automated online operation allows for

analysis of large sample sets.

We will present results from our systematic analysis of natural sediment/pore-water systems in coastal, open-ocean, and deeply-buried sedimentary environments. Our database on VFA isotopic composition reveals significant variability of $\delta^{13}\text{C}$ -acetate values in different geochemical regimes. For acetate, we observe a carbon isotopic range from -5 to -85‰, i.e., a similarly large range as known from methane. Highest values are associated with acetate consumption by acetoclastic methanogenesis while low values of -50‰, are linked to autotrophic production of acetate. A special case are samples from a methane seep environment where cycling of strongly ^{13}C -depleted carbon appears to affect the acetate pool, resulting in $\delta^{13}\text{C}$ values as low as -85‰. Our findings demonstrate that carbon isotopic compositions of VFAs are highly sensitive to various biogeochemical processes and can aid elucidation of carbon-flow patterns in microbial ecosystems.

Acknowledgements: The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the ACS Petroleum Research Fund.

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