



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 limited. The isotopic composition of acetate, an ubiquitous intermediate in anaerobic metabolism, is affected by biological processes that produce and/or consume it. Therefore, isotopic compositions 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. Our protocol requires only minor manipulation of the pore-water sample prior to analysis and avoids complex purification and derivatization steps. Our technique extends the previously accessible concentration range by more than an order of magnitude to lower concentrations and thus will enable systematic analysis of the variability of isotopic compositions in most sedimentary environments. Our field data and laboratory-based experiments indicate wide variations in the isotopic composition of acetate. For example, we find isotopic compositions to be generally lower in sulfate-reducing sediments than in methanogenic sediments. This presumably indicates that the carbon isotope effect associated with acetoclastic methanogenesis is higher than that associated with the consumption of acetate by sulfate-reducing microorganisms. We will present results from aqueous fluid samples that originate from coastal, open-ocean, and deeply-buried sedimentary environments. We will highlight the potential of VFA stable isotopes as indicators of predominant biogeochemical processes in natural environments.