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Compound-specific isotope analysis for assessing sources and fate of aromatic hydrocarbons in contaminated aquifers

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Organic compounds deriving from industry, oil spills, improper disposal and/or leaking storage tanks, landfill leachates, household use, motor vehicle emissions as well as agricultural fertilizers and pesticides are responsible for widespread soil and aquifer pollution. The fate and behavior of such compounds in the subsurface depend on a number of physicochemical and biological processes, which may lead to 'natural attenuation'. Determination and quantification of these processes are crucial for contamination risk assessment and sustainable groundwater management. Compound-specific isotope analysis (CSIA) by online-coupling of capillary gas chromatography and isotope ratio mass spectrometry (GC-IRMS) offers a versatile tool to study the origin and to assess degradation processes of organic pollutants in the environment.

The aim of the present work is to demonstrate the potential of CSIA for studying sources and fate of aromatic hydrocarbons in aquifer systems. Headspace solid-phase micro extraction (hsSPME) was applied as sample pre-concentration and extraction technique allowing for compound-specific carbon and hydrogen isotope analysis ($\delta^{13}\text{C}$ and δD) of volatile compounds, even at concentrations in the low ppb-range. The analytical approach was thoroughly evaluated in terms of its precision, linearity and reproducibility.

Our study focuses on carbon and hydrogen isotope fractionation of aromatic hydrocarbons such as benzene and toluene (BTEX), and the possibility how to evaluate biodegradation processes *in situ* according to the Rayleigh-equation. Results obtained at sites with two different contamination scenarios will be presented: The first location is situated at a former coal carbonization plant; the second site represents a typical contamination due to a leaking underground storage tank at a fuel station. In addition to the possibility for assessing the extent of biodegradation of organic contaminants in soil and groundwater systems, we will demonstrate how isotope signatures can help revealing different pollution sources. Limitations and challenging aspects of the method will be critically addressed.

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