



Monitoring *in situ* benzene biodegradation in contaminated aquifers using compound-specific stable isotope analysis (CSIA)

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Benzene is a groundwater pollutant of specific concern, since it causes a significant health risk due to its widespread occurrence, relatively high water solubility and toxicity. Biodegradation is the only *in situ* process leading to a decrease of benzene concentrations in groundwater coupled to a sustainable mass removal of the contaminant. Therefore, the evaluation of *in situ* biodegradation of benzene is essential for the implementation of groundwater management strategies such as Natural Attenuation (NA). In recent years, compound-specific stable isotope analysis (CSIA) has gained more and more attention as a tool for characterizing and assessing *in situ* biodegradation of organic pollutants in contaminated aquifers. This concept relies on the stable isotope fractionation occurring during the microbial degradation leading to an enrichment of heavier stable isotopes in the residual fraction of a contaminant. Thus, the observation of isotope ratio shifts for carbon, hydrogen or other elements that are involved in cleavage or generation of chemical bonds during the initial step of microbial transformation can be used as an indicator for *in situ* biodegradation. In the present study, CSIA was applied to investigate biodegradation of benzene within an aquifer located in the area of a former hydrogenation plant close to the city of Zeitz (Saxony-Anhalt, Germany). Based on multi-level sampling, we determined the vertical and horizontal distribution of carbon and hydrogen isotope ratios of benzene within the contaminant plume. Furthermore, the carbon and hydrogen isotope fractionation associated to microbial benzene degradation was investigated in laboratory experiments with anaerobic enrichment cultures from the field site and aerobic pure cultures. In

agreement with recently published studies, our results showed that aerobic and anaerobic benzene degradation lead to nearly the same carbon isotope fractionation but to significantly different hydrogen isotope fractionation. Hence, it is possible to distinguish between aerobic and anaerobic benzene biodegradation in the field by means of carbon and hydrogen isotope ratio analyses. Our field data provided evidence for anaerobic degradation of benzene especially at the fringe of the contaminant plume. Changes in carbon isotope ratios were used to quantify the *in situ* biodegradation of benzene using the Rayleigh equation. Furthermore, the applicability of the Rayleigh equation for the assessment of *in situ* biodegradation was investigated and showed limitations and advantages of this concept. In conclusion, our investigations show that CSIA is a useful tool for monitoring *in situ* biodegradation of benzene in contaminated aquifers.