Evolution of carbon isotope signatures during reactive transport of hydrocarbons in heterogeneous aquifers

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ABSTRACT

Compound-specific isotope analysis (CSIA) of organic pollutants has become a well-established tool for assessing the occurrence and extent of biodegradation processes in contaminated aquifers. However, the precision of CSIA is influenced by the degree to which assumptions underlying CSIA data interpretation hold under realistic field-scale conditions. For the first time this study demonstrates how aquifer analogs combined with reactive transport models offer an underexplored way to develop generic process understanding, evaluate monitoring and quantification strategies in highly heterogeneous subsurface settings. Data from high-resolution aquifer analogs were used in numerical experiments to track the propagation of a representative oxidizable organic compound (toluene) within a variety of realistic heterogeneous aquifers and to investigate its detailed fate. The simulations were used to analyze (1) the effects of physical aquifer heterogeneities on spatiotemporal patterns of contaminant concentrations and isotope signatures, (2) the performance of the commonly applied Rayleigh equation and (3) the applicability of an extension of the Rayleigh equation for complex hydrogeological conditions. The results indicate that if field-derived enrichment factors are applied without corrections for dilution, the conventional Rayleigh equation is inaccurate and estimates for biodegradation are typically overestimated and unreliable in heterogeneous aquifers. Underestimations can occur due to the partial source zone depletion. In contrast, if dilution can be accurately accounted for, field-derived enrichment factors comprise a suitable alternative to laboratory-derived and redox-specific enrichment factors. The study also examines to what extent variations in monitoring/sampling strategies influence the obtained results. Especially measurements from long-screened wells (>1 m) reveal to be inappropriate for the application of the Rayleigh equation in the investigated aquifer analogs, as low resolution data sampled from the simulated scenarios only enable a qualitative assessment of biodegradation. Measurements from both long- and short-screened wells employing the Rayleigh equation streamline approach are only partly viable for in situ biodegradation measurements in heterogeneous systems.

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1. Introduction

Over the last two decades monitored natural attenuation (MNA) has become the preferred option to manage aquifers

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polluted with organic contaminants, mostly due to the lack of alternative, truly cost-efficient active remediation technologies (Wiedemeier et al., 1999). As biodegradation is the only natural process that irreversibly reduces contaminant mass, its accurate quantification is essential for the evaluation of MNA effectiveness (e.g., Blum et al., 2009; Meckenstock et al., 2004). Biodegradation is typically accompanied by a measurable enrichment of heavier isotopes (e.g., ^{13}C, ^2H) in the non-degraded residual fraction of the contaminant. Therefore, compound-specific isotope analysis (CSIA) has become a regularly used tool to quantify biodegradation and to distinguish the extent of biodegradation from other concentration-attenuating processes in the field (D'Affonseca et al., 2011; Elsner, 2010; Elsner et al., 2005; Griebler et al., 2004; Meckenstock et al., 2004; USEPA, 2008; Van Breukelen and Prommer, 2008). CSIA relies on identifiable changes of stable isotope ratios (e.g., $\delta^{13}C$, δ^2H) and the extent of biodegradation is commonly quantified using the Rayleigh equation (Abe and Hunkeler, 2006; Blum et al., 2009; Elsner et al., 2005; Meckenstock et al., 2004). The key advantage of this approach is that it is easy-to-use. Strictly, the application of the Rayleigh equation requires a fully mixed and closed system where degradation is the only isotope fractionation process and can be expressed as:

$$\frac{R_t}{R_0} = \left(\frac{C_t}{C_0}\right)^{\alpha-1} \tag{1}$$

where C_0 and C_t denote the concentrations of a compound with the corresponding stable isotope ratios R_0 and R_t. The subscript indicates the time when the transformation reactions begins ($t = 0$) and any later time ($t > 0$). The extent of isotope fractionation is quantified by the isotope fractionation factor α. They are typically determined in laboratory experiments and reproducible (e.g., Sherwood Lollar et al., 1999; Slater et al., 2001). The isotope fractionation factor α can also be expressed as the enrichment factor ε, which is defined as $\varepsilon = 1000\,(\alpha - 1)$. However, the criteria for the Rayleigh equation are not always met under field conditions, where besides biodegradation other processes (e.g., dilution/dispersion) cause concentration changes (Mak et al., 2006).

Initial studies on the utilization of CSIA to assess in situ biodegradation of groundwater pollutants by Heraty et al. (1999), Hunkeler et al. (1999, 2000), Meckenstock et al. (1999) and Sherwood Lollar et al. (1999) already pointed out that isotope fractionation can be affected by physical processes such as dilution and sorption. Thus, the complexity of natural subsurface systems might limit the applicability of CSIA at field sites (Abrajano and Sherwood Lollar, 1999; Hunkeler et al., 2002).

Physical aquifer heterogeneity affects the fate of biodegrading compounds in various ways. For example, heterogeneity plays an important role on the shape and the time-scales of depletion of contaminant source zones (D'Affonseca et al., 2008; Fure et al., 2006). It is equally relevant for the geometry and longevity of the plumes that develop in the dissolved phase since non-uniform permeability distribution enhances mixing and thus accelerates biodegradation reactions (e.g., Bauer et al., 2009; Dentz et al., 2011; Werth et al., 2006). Consequently the biodegradation rates of dissolved contaminants can be highly variable during aquifer passage between the contaminant

source zone and downgradient sampling locations (e.g., Abe and Hunkeler, 2006; Stehmeier et al., 1999). Thus, a reliable quantification of the accumulated extent of in situ contaminant degradation becomes challenging (e.g., Braeckevelt et al., 2012; Fischer et al., 2007; Thullner et al., 2012; Van Breukelen and Prommer, 2008). For instance, in complex field situations CSIA-based in situ biodegradation estimates for BTEX compounds can be accompanied by relatively high uncertainties for a variety of reasons and accordingly restrict its applicability to being only a qualitative indicator (e.g., Van Keer et al., 2012).

Numerous non-destructive isotope-fractionating processes (e.g., dissolution, sorption, volatilization, diffusion) potentially impact biodegradation-induced shifts in isotope signals to a different degree (Braeckevelt et al., 2012). Processes previously believed to be non-isotope-fractionating were recently found to also cause fractionation such as dispersion and mixing (Eckert et al., 2012; Rolle et al., 2010; Van Breukelen and Rolle, 2012). Although dilution and mixing count as the most important non-destructive processes affecting Rayleigh equation based biodegradation estimates other non-destructive physical processes affecting reaction-induced isotope shifts have been reported (Thullner et al., 2012). They are considerably smaller than for biodegradation itself and potentially negligible for most sites (Thullner et al., 2012). Possible effects of small-scale mass transfer (Thullner et al., 2013), mass transfer from non-aqueous phase liquids to aqueous phase (Aeppli et al., 2009), sorption (Höhener and Atteia, 2010; Höhener and Yu, 2012; Kopinke et al., 2005; Van Breukelen and Prommer, 2008), volatilization (Kuder et al., 2009), and diffusion (Bouchard et al., 2008; LaBolle et al., 2008) on isotope fractionation and their impact on observed isotope signals has been demonstrated. Furthermore, Qiu et al. (2013) and Eckert et al. (2013) systematically investigated and discriminated the effects of biodegradation-induced, sorption-induced, and transverse-dispersion-induced effects on the overall isotope shift in a meso-scale tank experiment and reactive modeling study. Their results show that for process identification highly resolved data for concentrations and isotope ratios are required as well as reactive transport models that account for nonlinear degradation kinetics and isotope fractionation by reactive and physical processes.

Alternatively, CSIA-based quantification of biodegradation may also be carried out using numerical models, which allow for the consideration of more complex physical and chemical conditions, such as simultaneous occurrence of multiple degradation pathways and spatiotemporal variations of the aquifer's redox conditions (Atteia et al., 2008; D'Affonseca et al., 2011; Pooley et al., 2009; Prommer et al., 2009; Van Breukelen and Prommer, 2008; Van Breukelen et al., 2005). A range of recent studies have addressed the effects of aquifer heterogeneity on the reliability of biodegradation quantification by CSIA (Abe and Hunkeler, 2006; Fischer et al., 2006; Green et al., 2010; Kopinke et al., 2005; USEPA, 2008; Van Breukelen, 2007; Van Breukelen and Prommer, 2008), whereby both theoretical modeling studies of Abe and Hunkeler (2006) and Van Breukelen and Prommer (2008) concluded that physical heterogeneity may cause an underestimation of the extent of biodegradation if the Rayleigh equation is employed for data interpretation. However, these previous studies, which investigated the impact of physical heterogeneity on CSIA data interpretation, either were limited to investigations of simple,