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Assessment of the impact of pore-scale mass-transfer restrictions on microbially-induced stable-isotope fractionation

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ABSTRACT

Stable-isotope fractionation has become an established method for the assessment of contaminant biodegradation in groundwater. At the pore scale however, mass-transfer processes can limit the bioavailability of chemical species and therefore affect the observed fractionation. This can challenge the application of stable-isotope analysis in practice. A linear-exchange model provides a computational link between the microbially-induced isotope fractionation, determined under ideal conditions, and the fractionation observed under conditions of limited bioavailability. This simplifying conceptual approach allows for accurately estimating the mass-transfer limited degradation rates but its applicability for stable-isotope fractionation at the pore scale has not been evaluated yet. In this study, we perform high-resolution numerical simulations of microbial degradation and stable-isotope fractionation of a chemical species in a pore-scale model. The numerical results are compared to theoretical predictions derived from the linear-exchange model. Our results show an overall good agreement between numerical simulations and theoretical predictions, which confirms the applicability of the theoretical approach and of the value for the mass-transfer coefficient previously derived from the geometry of the pore space. In addition we provide a quantitative link between the value of the observable fractionation factor and the effective bioavailability of a biodegradable contaminant.

1. Introduction

The contamination of groundwater by hydrocarbon pollutants is one of the major problems for the drinking water supply in industrialized countries [1–3]. Due to the high burden involved in cleaning an aquifer, cost-effective methods like Natural Attenuation (NA) have gathered more interest [4–6]. The most desirable process contributing to NA is biodegradation, which – in contrast to other processes like sorption, dilution or volatilization – transforms the contaminant to harmless compounds instead of only lowering concentration values. In order to discriminate biodegradation from the other processes contributing to NA, Compound Specific Stable Isotope Analysis (CSIA) can be used [7–9]. This method is based on the observation that for many chemical compounds, reactive transformation rates (e.g. biodegradation) differ between different isotopologues, which leads to a fractionation of the isotopes. In contrast, the other aforementioned processes often cause only minor isotope fractionation and are commonly neglected [10,11]. As a result CSIA is nowadays widely accepted as a monitoring strategy for NA [12,9].

One of the challenges for the application of CSIA is that the fractionation factors, which best describe the situation in the field, may differ from the reference values determined under laboratory conditions [13–16]. One explanation, which has been proposed for this phenomenon, is the concept of limited bioavailability [17–20]. This means that a contaminant may not be fully available to the microorganisms for degradation. Under such circumstances the observed degradation is the result of two different processes: (i) a mass-transfer process (e.g. diffusion), which makes the contaminant available to the microorganisms and (ii) the actual degradation of the chemical compound by the microorganisms. The fractionation of this observed biodegradation will then depend on both the fractionation of the mass transfer and of the degradation.

Thullner et al. [21] derived a closed mathematical expression for the value of the observable fractionation factor under conditions of reduced bioavailability. For the microbial degradation rate, Michaelis–Menten kinetics [22] was assumed, whereas the mass-transfer step was modeled by a linear-exchange model [23,24]. In an associated study Kampara et al. [25] provided experimental evidence that a reduced bioavailability can affect the observed fractionation factor and therefore impact the application of CSIA in the field. A major problem, however, for the application of the

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Nomenclature

Latin

a_v	specific reactive surface $\left[\frac{1}{L}\right]$
B_{eff}	effective bioavailability (nondimensional)
c	concentration within the channel $\left[\frac{M}{V}\right]$
c_{bio}	bioavailable concentration within the channel $\left[\frac{M}{V}\right]$
c_{bulk}	averaged concentration within the channel $\left[\frac{M}{V}\right]$
D	matrix-diffusion coefficient $\left[\frac{L^2}{T}\right]$
K_{m}	half-saturation constant $\left[\frac{M}{V}\right]$
k_{max}	maximum reaction rate $\left[\frac{1}{T}\right]$
k_{tr}	mass-transfer coefficient $\left[\frac{1}{T}\right]$
Pe	Péclet number (nondimensional)
R	isotope composition (nondimensional)
r_{tot}	reaction rate $\left[\frac{M}{V\,T}\right]$
r_{reac}	reaction rate $\left[\frac{M}{V\,T}\right]$
$\mathbf{v}$	fluid velocity in the channel $\left[\frac{L}{T}\right]$

Greek

α	isotope fractionation factor (nondimensional)
α_{reac}	reaction-induced fractionation factor (nondimensional)
α_{tr}	mass-transfer-induced fractionation factor (nondimensional)
α^*	observable fractionation factor (nondimensional)
Φ^2	Thiele modulus (nondimensional)

miscellaneous

${}^{l}[\cdot]$	quantities with respect to the light isotope
${}^{h}[\cdot]$	quantities with respect to the heavy isotope
$[\cdot]_0$	quantities at the inlet of the channel
$[\cdot]_{\text{ref}}$	reference quantity
$\hat{[\cdot]}$	non-dimensional quantity

equation provided by Thullner et al. [21] is the determination of the parameters occurring therein. For Michaelis–Menten kinetics, parameter values can be found in the literature [26–28]. Within the context of isotope fractionation no such procedure exists for the linear-exchange model used for the description of the mass transfer. Furthermore, the linear-exchange model describes mass transfer between two distinct reservoirs each with a single concentration value of a chemical compound. By contrast, in porous media (and many other environments) the mass transfer controlling the bioavailability of a chemical compound occurs along concentration gradients describing gradual concentration changes not suggesting an obvious separation into two reservoirs. As a result, the application of this mathematical expression for practical applications might be seriously hampered.

In a recent study by Hesse et al. [29] it has been shown only for effective degradation rates that such a linear-exchange model can be used to provide reasonable estimates for conditions affected by bioavailability restrictions. These authors further showed that it is possible to parameterize the model by a single constant parameter, while still being able to reproduce the observed degradation behavior with acceptable errors (i.e., degradation rate estimation errors of $\leqslant 10\%$). Despite the similar setup, both of these studies investigate different phenomena leading to structurally different descriptions for the quantity under consideration (the observable fractionation factor in [21] and the effective reaction rates in [29]). It is consequently not clear if these acceptable errors, reported by Hesse et al. [29], will lead to equally good results in case of stable-isotope fractionation and if parameter estimates derived by Hesse et al. [29] for the mass-transfer process are equally applicable for quantitatively describing mass-transfer effects on observable stable-isotope fractionation factors. This is specifically relevant given that the relative differences leading to isotope fractionation are in the range of ‰ requiring these differences to be described at high accuracy. Another limitation of the expression presented by Thullner et al. [21] is the confinement on biodegradation as the only fractionating process. Although usually of less relevance, other processes like sorption [30], volatilization [31] or diffusion [32] can be fractionating as well. In contrast to microbial degradation, where the fractionation is caused by different energy levels needed to break up the chemical bonds of the contaminant [33], diffusion is fractionating due to the different specific mass of different isotopologues [34]. Specific values for either fractionation factor may differ from species to species. Diffusion-induced fractionation is usually smaller than microbially-induced fractionation [35], but Rolle et al. [36] could show that, although in different context, diffusive fractionation can have a major impact on larger scales and should therefore be taken into consideration [36–38].

In this study we therefore investigated if the constant parameter derived by Hesse et al. [29] can be used for the parametrization of the expression derived by Thullner et al. [21], too. To that end we used a numerical setup similar to the one described by Hesse et al. [29], which was expanded in order to feature the effect of isotope dependent biodegradation. This numerical setup was used to determine (i) if the linear-exchange model, successfully applied by Hesse et al. [29], is also sufficient to quantitatively describe mass-transfer-limited stable-isotope fractionation at the pore scale, (ii) if, in case the linear-exchange model is applicable, the constant estimate of the coefficient of the linear-exchange model of Hesse et al. [29] can be used to predict the changes of the observable stable-isotope fractionation and (iii) if the analytical expression of Thullner et al. [21] can be expanded to account also for the fractionating effect of the diffusive mass transfer. Furthermore, the results of this study were used to establish a quantitative link between observable stable-isotope fractionation and the effective bioavailability of a compound, which allows predicting bioavailability-induced rate limitations from stable-isotope data.

2. Theory

2.1. Quantifying stable-isotope fractionation

The basis of the quantitative description of stable-isotope fractionation is the fractionation factor α, defined as

$$\alpha = \frac{{}^{h}r_{\text{reac}}}{{}^{l}r_{\text{reac}}}\frac{{}^{l}c}{{}^{h}c} = \frac{{}^{h}r_{\text{reac}}}{{}^{l}r_{\text{reac}}}\frac{1}{R}. \tag{1}$$

Here ${}^{h}r_{\text{reac}}$ and ${}^{l}r_{\text{reac}}$ are the reaction rates of the heavy and light isotope and ${}^{h}c$ and ${}^{l}c$ are the respective isotope concentrations of the reactant. Due to the preferential degradation of the lighter isotope the composition R in the residual concentration of the chemical reactant is changing along the flow path.

A common approach for the assessment of isotope fractionation is the well known Rayleigh equation [39], which is widely used for the interpretation of kinetic isotope-fractionation processes (although several alterations have been proposed [40–43]). This equation is defined in its logarithmic form as