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RESEARCH ARTICLE

Analytical transport modelling of metabolites formed in dual-porosity media

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Abstract Contaminants like nitroaromatic compounds can be degraded in the subsurface to similar or even more toxic metabolites. Degradation or transformation rates are dependent on physical, chemical and biological properties which can be different in sedimentological layers or other heterogeneous structures of aquifers. Sediments with low hydraulic conductivity can even consist of immobile water. These regions are only accessible by diffusion. Most modelling approaches accounting for immobile water regions focused on the mathematical description of the transport and decay of the parent compound. The objective of this study was to develop an analytical model to quantify the transport and formation of a metabolite in dual-porosity media describing the exchange between mobile and immobile water regions based on the metabolite's diffusion coefficient. Column experiments with a well-defined immobile water region were performed under anoxic conditions at three different water flow velocities. The model compound 4-Cl-nitrobenzene was reduced to 4-Cl-aniline (4-Cl-An) by surface-bound Fe (II) species within the immobile water region. Transport and formation of the metabolite were quantified with a modified solution of the single fissure dispersion model assuming additionally for the region with immobile water first-order metabolite production, irreversible sorption and an instantaneous equilibrium sorption.

The number of unknown fitting parameters was reduced to two (sorption rate and retardation factor) by stepwise parameter estimation using tracer and parent compound data. Experimental results of the metabolite for each water flow velocity were successfully described with a first-order production term ($\lambda_{\text{prod}} = 1.51 \pm 0.08$ h^{-1}), retardation factor ($R_{\text{im}} = 2.94 \pm 0.45$) and first-order irreversible sorption rate ($K_{\text{im}} = 0.39 \pm 0.16$ h^{-1}) within the immobile water region. Model results supported that 4-Cl-An was formed within the immobile water region. 4-Cl-An sorbed instantaneously onto the clay matrix while a fraction was irreversibly sorbed. Experimental results and the provided analytical solution help to improve the understanding about reactive transport and the formation of metabolites in dual-porosity media.

Keywords Reactive solute transport · Nitroaromatic compounds · Analytical modelling · Matrix diffusion · Metabolite · Transformation · Dual-porosity column experiment · Immobile water

Introduction

Various contaminants are transformed to similar or even more toxic metabolites in the subsurface. Compounds can be transformed by biological degradation, chemical reactions or radioactive decay. Formed metabolites are either stable or are further degraded until mineralization. Transport of contaminants is driven by advection and dispersion and is influenced by sorption onto the aquifer's material. Reactive transport in homogeneous aquifers is well understood, but remains challenging in heterogeneous aquifers. Here, the fate of solutes is further influenced by the aquifer's heterogeneity and dynamic flow conditions. A high contrast in permeability between sedimentological layers or due to any other structural

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heterogeneity creates the so called dual-porosity systems with regions containing either mobile or immobile water (Barenblatt et al. 1960, Warren and Root 1963). Solutes can exchange between these two regions driven by diffusion. Immobile water regions have a high storage capacity with different physical, chemical and biological properties in comparison to mobile water regions. This can influence the retention and decay of contaminants which is of relevance in fractured, karst and aquifer-aquitard systems (Foster 1975; Grisak and Pickens 1980; Neretnieks 1980; Tang et al. 1981).

Immobile water regions are of special interest for evaluating the fate of nitroaromatic compounds (NACs) in the subsurface (Fesch et al. 1998). NACs are used as solvents and intermediates in the synthesis of dyes, pesticides and explosives and have been accidently released to the environment since World War I (Rodgers and Bunce 2001; Thieme 1996). The problem is that NACs are reduced by Fe (II) species bound on clay minerals (Elsner et al. 2004; Hofstetter et al. 1999; Hofstetter et al. 2003) to similar or even more toxic anilines. The above-mentioned authors showed that the abiotic reaction only takes place under anoxic conditions, at surfaces and at the presence of structural and surface-bound Fe (II) species. Therefore, this reaction is most likely to occur in regions with high clay contents and thus might be an important process in the presence of immobile water regions, too.

Transport of 4-chloronirtobenzene (4-Cl-Nb; by-product in the TNT production) in dual-porosity column experiments at different water flow velocities was quantified with an extended analytical model based on the single fissure dispersion model (SFDM) developed by Maloszewski and Zuber (1985, 1990) in Knorr et al. (2016a). The extended model accounted for abiotic reduction of 4-Cl-Nb to 4-chloroaniline (4-Cl-An) by structural and surface-bound Fe (II) species following first-order kinetics (Elsner et al. 2004; Hofstetter et al. 1999; Hofstetter et al. 2003) and an instantaneous sorption onto clay minerals within the immobile water region (Haderlein and Schwarzenbach 1993; Haderlein et al. 1996). Fitted parameters from tracer data were further used as an input parameter to quantify transport of 4-Cl-Nb (Knorr et al. 2016a). A retardation factor and first-order reaction rate were the only remaining fitting parameters. Both sorption and the abiotic reduction occurred only within the immobile water region. On the one hand, sorption enhanced the mass exchange from mobile to immobile water region. On the other hand, the reduction by structural and surface-bound Fe (II) species inhibited the back diffusion. An estimated retardation factor and reaction rate were consistent under different flow conditions indicating the independency of those parameters on water flow velocity. Still, the transport of the metabolite remained unknown.

Generally, the mathematical prediction of metabolite fluxes in dual-porosity media remains challenging due to the high number of fitting parameters (dispersion, transit time,

diffusion, reaction/production rate and sorption) which increases the uncertainty in parameter estimation. However, the number of fitting parameters can be reduced by applying ideal tracers with different molecular diffusion coefficients to characterize a dual-porosity system. Tracers are transported by advection and dispersion in the mobile water region with a diffusive mass exchange into the immobile water region. The exchange is dependent on the tracer's diffusion coefficient. This results in different maximum peak concentrations and mass recoveries between different tracers. A back diffusion from immobile to mobile water regions causes pronounced tailings. The advantage of applying tracers with different diffusion properties is that estimated fitting parameters can be indirectly validated by comparing model results for each tracer (Knorr et al. 2016b). Estimated parameters can then be used as input parameters to further describe reactive transport.

The mathematical quantification of these processes could be realized by using various available numerical flow and transport models (e.g. Feflow, Modflow, HydroGeoSphere, PHREEQC). However, the fact that the spatial distribution of immobile water regions is mostly unknown complicates the applicability of such models. Further, a computing time consuming fine temporal and spatial discretization is needed to adequately simulate the diffusive mass exchange without causing numerical dispersion (Chapman et al. 2012). In contrast, analytical models with constant initial and boundary conditions give exact solutions based on physical principles, and less computing time is needed. They can also be applied to a system with unknown structures of immobile water regions. However, only few analytical models are available accounting for the formation of a compound of interest in dual-porosity media and accounting for mass exchange between compartments. In doing so, there are two main concepts in describing the diffusive mass exchange between mobile and immobile water region. Either it is described with an empirical first-order transfer parameter (Field and Leij 2014; Leij and Bradford 2009; Bauer et al. 2001; Fesch et al. 1998; Toride et al. 1999; Toride et al. 1993) or taking into account the solutes molecular diffusion coefficient (Sudicky and Frind 1984). Different model approaches were compared for identifying the importance of immobile water zones in rather homogeneous sediments (Haggerty and Gorelick 1995). Here, transport was best described using a mixture of diffusion rate coefficients in comparison to a first-order rate approach. Toride et al. (1993) developed an analytical solution for transport in dual-porosity media accounting for first-order decay, zero-order production and sorption in both regions. The exchange between these regions is described as a first-order process. An analytical solution for transport of a decay chain in homogenous porous media was extended to dual-porosity media by Bauer et al. (2001). Parent compound and metabolites are coupled by first-order decay processes assuming linear equilibrium sorption in both regions. The diffusive exchange between

the regions was described with an empirical first-order parameter and not considering the solute's molecular diffusion coefficient.

Sudicky and Frind (1984) developed an analytical solution for two-member radionuclide decay chain during transport through a single fracture. In contrast to the models mentioned above, this solution describes mass exchange between mobile and immobile water regions based on the solute's molecular diffusion coefficient. Thus, it has a physical meaning in contrast to empirical fitted parameters. The model accounts also for sorption both in the fracture and the porous matrix, but it neglects dispersion within the mobile water region. The solution is further only valid for a continuously contaminant input. A similar approach was presented by Fesch et al. (1998) using Fick's first law, and thus, diffusion coefficients account for solute exchange between immobile and mobile zones. This approach also accounts for sorption, but neither degradation nor metabolite formation has been included.

Therefore, an analytical model is required for instantaneous injection of the parent compound that accounts for the metabolite production within the immobile water region and that describes mass exchange based on the molecular diffusion coefficient. Knorr et al. (2016a) only focused on the transport of the parent compound 4-Cl-Nb, but the transport of the formed metabolite 4-Cl-An has not been quantified yet.

The aim of this study was to develop an analytical solution based on the SFDM model approach (Maloszewski and Zuber 1985, 1990) to quantify the formation and the transport of 4-Cl-An in dual-porosity column experiments. The number of unknown fitting parameter is reduced by using stepwise estimated transport parameters from both tracer and parent compound data from a previous study (Knorr et al. 2016a). The quantification of processes can help to improve the understanding on the fate of metabolites in heterogeneous aquifers. This is of concern because metabolites are eventually more stable and similar or even more toxic than the parent compounds.

Material and methods

The experimental design and applied methods were previously described in Knorr et al. (2016a). Additionally to the already presented data, we focus on the observed 4-Cl-An (metabolite) concentrations in this study.

Chemicals

4-Cl-Nb, 4-Cl-An, 4-(2-hydroxyethyl) piperazine-1-ethanesulfonic acid (HEPES), iron (II) chloride (FeCl2) and potassium bromide (KBr) were purchased from Sigma-Aldrich (St. Louis, USA). Deuterium-labelled water (92.0 atom%) was purchased from Chemotrade (Leipzig, Germany).

Dual-porosity column experiments

The acryl column (height 50.8 cm, inner diameter 9.0 cm) was packed with coarse quartz sand surrounded by clay creating well-defined mobile and immobile water regions (Fig. 1). The cylindrical mobile water region (quartz sand) had a diameter of 4.8 cm. For filling, a thin installation tube with an external diameter of $\phi_{in} = 50$ mm was set into the centre of the column. First, the annular space between column and installation tube was filled with some water. Dry clay powder was added to the annular space. Water and clay were homogenized using a rod. This procedure (adding alternatively water and clay) was repeated until the column was filled to the top. The installation tube was removed after packing. Dry quartz sand was placed into the centre of the column and sequentially saturated.

A porosity n_m of 0.44 ± 0.01, a hydraulic conductivity of 7.0×10^{-3} m s^{-1} and a grain size distribution ranging between 1 and 1.8 mm were determined for the coarse quartz sand (Dorsilit Nr. 5F, Quarzsande GmbH, Germany). Porosity was calculated from the mass of sand for filling the column, grain size distribution was determined through sieving and hydraulic conductivity was measured with the constant head method (Klute and Dirksen 1986). The clay (Compactonit 10/80, GWE Pumpenboese GmbH, Germany) had a porosity n_{im} of 0.56 ± 0.01, which was determined through weighing saturated
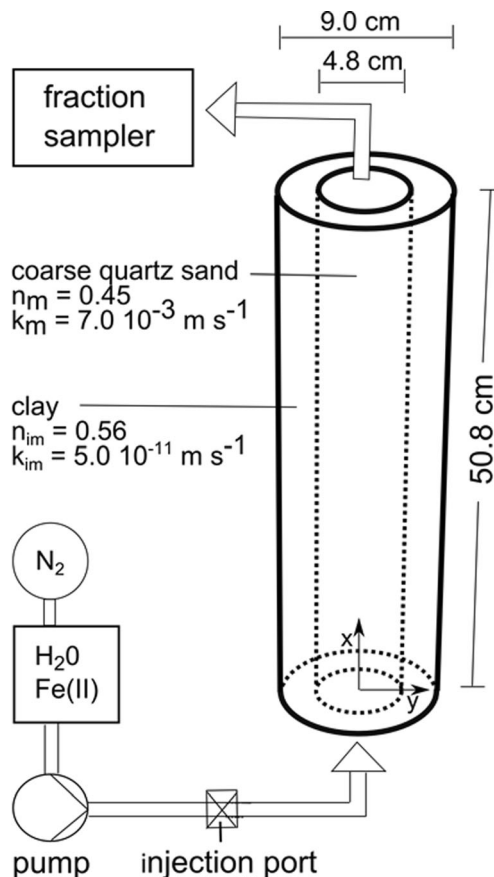

Fig. 1 Experimental design of the dual-porosity column experiment

and dry clay in a cylinder with known volume. Hydraulic conductivity (5.0×10^{-11} m s^{-1}) was determined with the falling head method. The grain size distribution was 2% sand, $19 \pm 3\%$ silt and $79 \pm 3\%$ clay, and the mineral composition of the fraction with a grain size classified as clay was 17% quartz, 37% kaolinite, 11–14% smectite and 7–10% other swelling clay minerals, both according to the supplier (GWE Pumpenboese GmbH, Germany).

Experiments were conducted under saturated and anoxic conditions. Nitrogen connected to the water reservoir (Milli-Q, MilliporeElix + Milli-Q Advantage 10A, USA, with 10 mM HEPES, 1.0 M Fe (II) and pH 6.9 adjusted with KOH) ensured anoxic condition during the experiments. Stainless steel tubing was used. An O$_2$-sensitive foil (PSt3, Fibox 3, PreSens, Regensburg, Germany) installed at the column wall was applied to measure the O$_2$ concentration for giving evidence about anoxic conditions within the column which was reached after 2 weeks of flushing. The flow direction was from the bottom to the top of the column. A peristaltic pump (Gilson Abimed Minipuls 3) was applied to provide a constant flow. Outflow was sampled with an autosampler (Model LF10 5M, Ma Ron GmbH, Germany) in regular time intervals.

In total, three experiments were conducted at water flow velocities of 1.0 m day^{-1}, 0.6 m day^{-1} and 0.3 m day^{-1} in the following referred to as experiment A, B and C, respectively. A summary of experimental conditions is given in Table 1. Two conservative tracers (bromide and deuterium) with different molecular diffusion coefficients were applied to characterize the dual-porosity system. Tracers and 4-Cl-Nb were injected simultaneously in a short pulse (Dirac-Impulse) over the whole cross section of the mobile water region. In the present setup, the metabolite 4-Cl-An can only be formed by the reduction of 4-Cl-Nb in the presence of structural and surface-bound Fe (II) species and thus in the immobile water region. Fractions of water samples were collected at the column outlet and analysed for 4-Cl-An using a high-performance liquid chromatograph HPLC (LC-10A, Shimadzu) applying a PFP column (2.6u PFP 100A 75 × 4.6 mm, Phenomenex, Aschaffenburg, Germany). One hundred microlitres of a sample was injected. Methanol and water (50:50) were used as a solvent at a flow rate of 1.0 ml min^{-1}. 4-Cl-An was quantified by UV absorbance at a wavelength of 254 nm.

Mathematical modelling

The transport of both tracers and the parent compound 4-Cl-Nb was previously quantified with an analytical model in Knorr et al. (2016a). In this study, we present a new model describing transport of metabolites formed in the immobile water region. The formation and transport of 4-Cl-An were modelled by developing an analytical solution based on the SFDM presented by Maloszewski and Zuber (1985, 1990). It is important to note that this model application should not be limited to describe transport in laboratory systems with known geometry and properties. In contrast, the column system was only chosen to validate the model in porous systems. The ultimate goal is to use the model approach also in field studies where the distribution and properties of the immobile water zone are unknown. In combination with multi-tracer experiments, it has the potential to estimate properties of the immobile and mobile water fraction as well as to simulate reactive transport.

The conceptual model of transport processes for 4-Cl-An is illustrated in Fig. 2. 4-Cl-An is formed due to the abiotic reduction of 4-Cl-Nb by structural and surface-bound Fe (II) species within the immobile water region. The reduction of 4-Cl-Nb follows pseudo first-order kinetics. The production rate of 4-Cl-An is assumed to be identical to the reduction rate of 4-Cl-

Table 1 Experimental conditions and parameters estimated from tracer and parent compound taken from Knorr et al. (2016a)

Known parameter	Unit	Experiment		
		A	B	C
Volumetric flow rate Q	mL h^{-1}	31.8	18.6	9.8
Water flow velocity v	m day^{-1}	1.0	0.6	0.3
4-Cl-Nb injected	mg	0.31	0.33	0.31
Injection volume	mL	3	3	3
Injection time	min	5.7	9.7	18.4
Total experiment time	h	18	55	90
Parameters estimated from tracers				
Mean transit time t_0	h	12.1	21.3	38.5
Dispersion parameter P_D	–	0.0012	0.0013	0.0010
Diffusion parameter $a_{Deuterium}$	s$^{-1/2}$	1.16×10^{-3}	1.13×10^{-3}	$1.13 \cdot 10^{-3}$
Parameters estimated from 4-Cl-Nb				
First-order reaction rate $k_{4\text{-Cl-Nb}}$	h^{-1}	1.60	1.47	1.45

Fig. 2 Conceptual model of 4-Cl-An transport in dual-porosity media
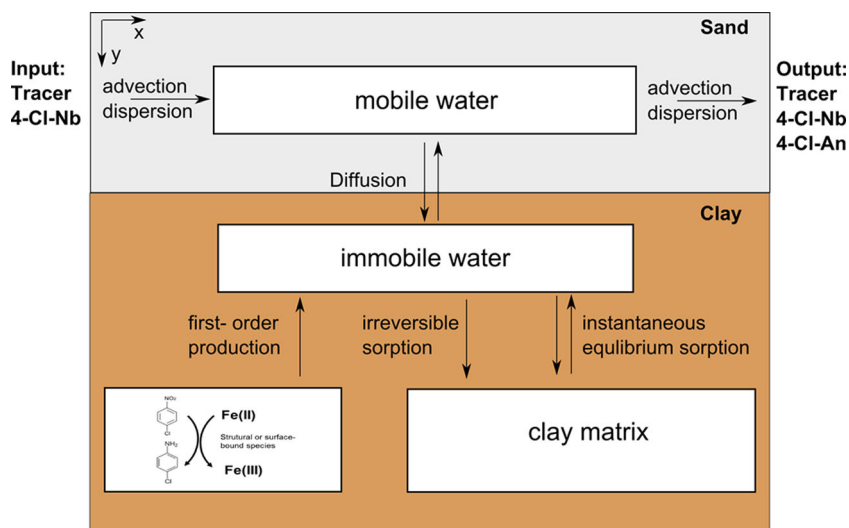
Nb and can be described as the following:

$$ClC_6H_4NO_2 + 6\,e^- + 6\,H^+ \rightarrow ClC_6H_4NH_2 + 2\,H_2O \quad (1)$$
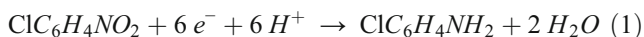
An instantaneous sorption and an irreversible kinetic sorption process are assumed to occur onto the matrix of the immobile water region. The mass exchange between mobile and immobile water region is driven by diffusion. In the mobile water region, transport is dominated by advection and dispersion. Sorption onto quartz sand in the mobile water region is assumed to be negligible (Haderlein and Schwarzenbach 1993).

On the basis of Maloszewski and Zuber (1985, 1990), the conceptual model in Fig. 2 can be mathematically described by the following equations:

$$\frac{\partial C_m}{\partial t} + v\frac{\partial C_m}{\partial x} - D\frac{\partial^2 C_m}{\partial x^2} - \frac{n_{im}D_{im}}{2b}\frac{\partial C_{im}}{\partial y}\bigg|_{y=-\frac{\phi_{in}}{2}} = 0 \quad \text{for } 0 \le y < \frac{\phi_{in}}{2}$$
$$(2)$$

$$C_{im}(t) = [C_m(t)]_{pc}\left[1 - e^{-\lambda_{prod}t}\right] \qquad \text{for } \frac{\phi_{in}}{2} \le y < \infty \quad (3.1)$$

$$R_{im}\frac{\partial C_{im}}{\partial t} - D_{im}\frac{\partial^2 C_{im}}{\partial y^2} - K_{im}C_{im} = 0 \qquad \text{for } \frac{\phi_{in}}{2} \le y < \infty$$
$$(3.2)$$

where C_m and C_{im} are the metabolite concentrations in the mobile and immobile water region [M L^{-3}], $[C_{im}]_{pc}$ is the concentration of the parent compound in the immobile water region [M L^{-3}], v is the mean water velocity [L T^{-1}], D is the dispersion coefficient [L^2 T^{-1}] in the mobile water region, ϕ_{in} is the diameter of the mobile water region [L], n_{im} is the porosity of the clay matrix [−], x is the flow distance and the axis of the main flow direction (cylinder axis) [L] and y is the distance perpendicular to the main flow axis [L]. D_{im} is the effective diffusion coefficient in the immobile water region (molecular diffusion coefficient D_0 divided by the tortuosity $\tau = 1.5$ (tortuosity was calculated accordingly to Boudreau (1996)) [L^2 T^{-1}], R_{im} is the instantaneous retardation factor [−], λ_{prod} is a first-order production rate of the metabolite [T^{-1}] which is equal to the first-order decay rate of the parent compound and K_{im} is the irreversible kinetic sorption rate of the metabolite in the immobile water region [T^{-1}].

Initial and boundary conditions are identical as described previously in Maloszewski and Zuber (1985, 1990). A solution for a Dirac injection with these initial and boundary conditions is given by the following equation modified after Maloszewski and Zuber (1985, 1990):

$$C_m(t) = \frac{M\,a\sqrt{R_{im}}}{2\pi Q}\sqrt{\frac{t_0}{P_D}}\left\{\int_0^t exp\left[-\frac{(t_0-u)^2}{4P_Dut_0} - \frac{\left(a\sqrt{R_{im}}\right)^2u^2}{t-u} - \frac{K_{im}}{R_{im}}(t-u)\right]\frac{du}{\sqrt{u(t-u)^3}} - \int_0^t exp\left[-\frac{(t_0-u)^2}{4P_Dut_0} - \frac{\left(a\sqrt{R_{im}}\right)^2u^2}{t-u} - \frac{K_{im}+\lambda_{prod}}{R_{im}}(t-u)\right]\frac{du}{\sqrt{u(t-u)^3}}\right\}$$
$$(4)$$

where M is the mass of the metabolite [M] which can evolve from the mass of the injected parent compound M_{pc} [M], a is called a "diffusion parameter" [T$^{-1/2}$] including geometrical

properties of the system and the solute's effective diffusion coefficient D_{im} in the immobile water region [L^2 T^{-1}], R_{im} is an instantaneous retardation factor [−], Q is the volumetric flow

rate [L^3 T^{-1}], t_0 is the mean transit time of mobile water [T], P_D is the dispersion parameter [−], u is an integration variable, t is the time after injection [T], λ_{prod} is the first-order production term [T^{-1}] and is equal to the first-order decay rate of the parent compound and K_{im} is the irreversible kinetic sorption rate of the metabolite in the immobile water region [T^{-1}].

Theoretically, the transport Eqs. (2) and (3.2) require the same (or similar) retardation and diffusion properties (R_{im} and D_{im}) for pollutant and metabolite. However, for the solution of Eq. (4), it is sufficient that the R_{im} and the product of $D_{im} \times R_{im}$ for the metabolite are more or less equal to that of the pollutant which is a valid assumption due to similar chemical structures of product and metabolite in this study.

Equation (4) contains six unknown fitting model parameters: mean transit time of water (t_0), dispersion parameter (P_D), diffusion parameter (a), retardation factor (R_{im}), first-order production term (λ_{prod}) and irreversible kinetic sorption rate (K_{im}).

$$t_0 = \frac{V_m}{Q} \tag{5}$$

$$P_D = \frac{\alpha_L}{L} \tag{6}$$

$$a = \frac{n_{im}\sqrt{D_{im}}}{2b} \quad \text{with} \quad 2b = \Phi_{in}\, n_m \tag{7}$$

$$R_{im} = 1 + \frac{1-n_{im}}{n_{im}}\rho_{im}k_d \tag{8}$$

where V_m is the volume of mobile water in the system [L^3], α_L is the longitudinal dispersivity [L], L is the column length [L], k_d is sorption coefficient [L^3 M^{-1}] and ρ_{im} is the dry bulk density of clay material [M L^{-3}].

Ideal tracers were used to estimate the mean transit time, dispersion and the diffusive mass exchange between mobile and immobile water regions. Mean transit time and dispersion parameter are identical for conservative and reactive transport. The diffusion parameter a, describing the diffusive mass exchange between mobile and immobile water regions, was adjusted accordingly to the molecular diffusion coefficient of the reactive compound:

$$a_{meta} = \frac{\sqrt{D_{im(meta)}}}{\sqrt{D_{im(tracer)}}}\, a_{tracer} \tag{9}$$

where a_{meta} is the diffusion parameter of the metabolite and $D_{im(meta)}$ the effective diffusion coefficient of the metabolite 4-Cl-An (0.67 × 10^{-9} m s^{-2}) in the immobile water region. The effective diffusion coefficient of the tracer (deuterium) was 1.6 × 10^{-9} m s^{-2}. Using these parameters as model input, the first-order reaction rate and a retardation factor was then estimated for 4-Cl-Nb in Knorr et al. (2016a). Mean transit time, dispersion and the diffusion parameter estimated from tracer data and first-order reaction rate estimated from the parent compound were used to reduce the number of fitting parameters for

4-Cl-An. A summary of those previously estimated input parameters in Knorr et al. (2016a) is given in Table 1.

The first-order decay rate of 4Cl-Nb is assumed to be identical to the first-order production term λ_{prod} of the metabolite 4-Cl-An. Thus, the only remaining fitting parameters to describe transport of 4-Cl-An are the retardation factor R_{im} and the irreversible kinetic sorption rate K_{im}.

Transport was modelled by fitting Eq. (4) by a trial-and-error procedure to observe data. The goodness of the fitting is given by the Nash-Sutcliffe coefficient E [−] (Nash and Sutcliffe 1970):

$$E = \left[1 - \frac{\sum_{i=1}^{N}\left(C_f^i - C_{obs}^i\right)^2}{\sum_{i=1}^{N}\left(C_{obs}^i - C_{mean}\right)^2} \right] \times 100\% \tag{10}$$

$$C_{mean} = \sum_{i=1}^{N}\frac{C_{obs}^i}{N} \tag{11}$$

where C_{obs}^i is the observed concentration [M L^{-3}] at time t_i [T], C_f^i is the fitted concentration [M L^{-3}] at time t_i [T], C_{mean} is the mean value of observed concentrations [M L^{-3}] and N is the number of observations [−]. This method enables a direct comparison of the quality of the model calibration between singular experiments performed with different injected tracer masses.

To improve the fitting procedure, relative recovery rates, RR (t), were calculated from the experimental data over time (t) and compared with those calculated from the fitted curve (Maloszewski and Zuber 1990):

$$RR(t) = \frac{M_{pc}Q}{M_m m_{pc}}\int_0^t C(t)dt \tag{12}$$

where C (t) is the concentration [M L^{-1}] equal to $C_{obs}(t)$ or $C_m(t)$ for calculating experimental and fitted recoveries, respectively. M_{pc} is the molecular weight of the parent compound [4-Cl-Nb 157.55 g mol^{-1}], M_m is the molecular weight of the metabolite [4-Cl-An 127.57 g mol^{-1}] and m_{pc} is the injected mass of the parent compound [M]. Taking into account proposed improvement of calibration procedure by simultaneous fitting metabolite concentration C (t) and recovery curves RR (t), the solution (estimated parameters) for the model becomes unique.

Results and discussion

Observed breakthrough curves

Relative mass recoveries and breakthrough curves (BTCs) obtained from experiment A, B and C are plotted versus relative time (time t divided by the mean transit time t_0) in Fig. 3. Observed concentrations of 4-Cl-An were normalized to the
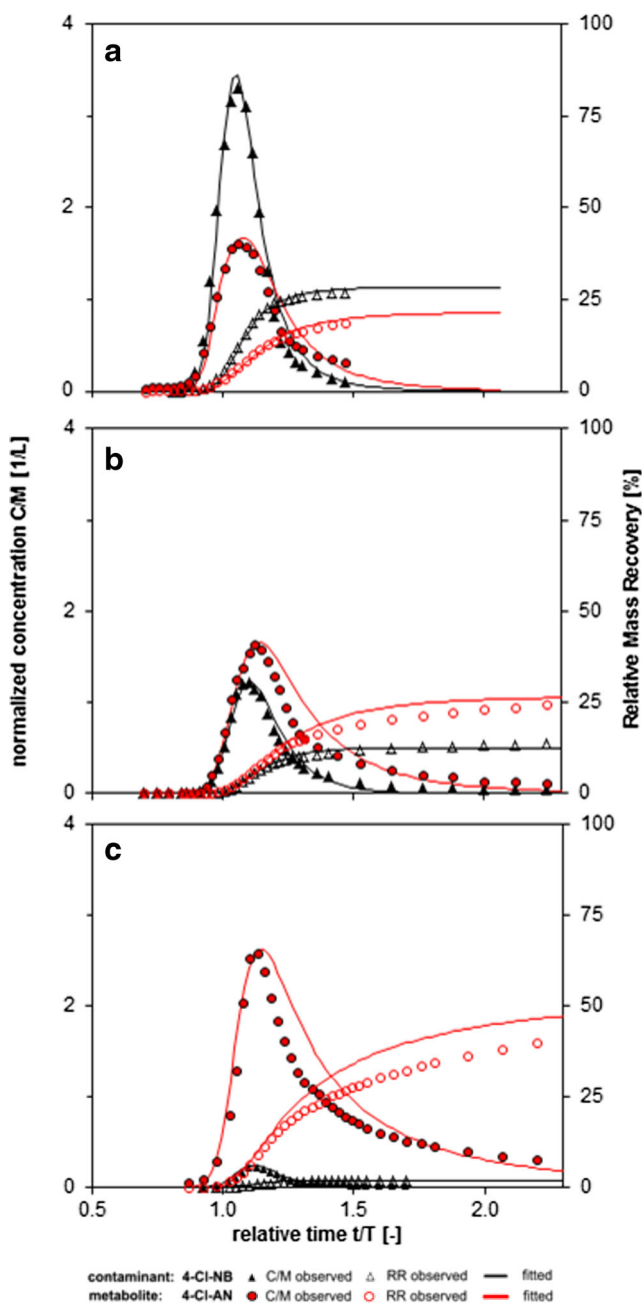
Fig. 3 Observed and fitted BTCs of bromide, deuterium and 4-Cl-Nb in experiment A (a), B (b) amd C (c). Normalized concentration C M^{-1} is plotted versus relative time t T^{-1}; concentration curves from 4-CL-Nb were taken from Knorr et al. (2016a)

mass evolving from the complete transformation of injected 4-Cl-Nb to 4-Cl-An.

BTCs of 4-Cl-An were found to peak at the same time as conservative tracers (data not shown) and 4-Cl-Nb in each experiment. Pronounced tailings were observed caused by the diffusive mass exchange between mobile and immobile water region. In contrast, only little to no tailings was observed for 4-Cl-Nb. Normalized maximum peak concentration was identical in experiment A and B (1.6 L^{-1}) and

increased to 2.8 L^{-1} in experiment C. The maximum peak concentration of 4-Cl-Nb was higher in experiment A and lower in B and C in comparison to 4-Cl-An. Relative mass recovery increased with decreasing water flow velocity after the same relative time of 1.5. A recovery of 18.2, 18.3 and 28.9% was found for experiment A, B and C, respectively. The relative mass recovery of the parent compound 4-Cl-Nb decreased with decreasing water flow velocity (26.7, 11.9, 1.8%) after the same relative time of 1.5. The timing of the maximum peak concentration of 4-Cl-An was identical in comparison to tracers and parent compound. Identical peak times of metabolite and tracers indicated that the metabolite was not adsorbed onto quartz sand.

Modelling results

Observed and fitted BTCs and mass recoveries are plotted in Fig. 3. Fitted retardation factor R_{im} and irreversible kinetic sorption rate K_{im} for 4-Cl-An of each experiment are summarized in Table 2. The model successfully described the transport of 4-Cl-An accounting for a first-order production within the immobile water region and an instantaneous equilibrium sorption onto the clay assuming that a certain amount of 4-Cl-An was even irreversibly sorbed.

The model calibration was performed by using input parameters obtained from tracer and parent compound data. Parameters estimated from tracers were not only calibrated but also directly and indirectly validated yielding independently known parameters with very good accuracy. From fitted parameters, calculated porosities of both regions and the mobile water volume had an accuracy of 5% to directly measured values (Knorr et al. 2016b). Direct validation indicated that any error caused by neglecting radial diffusion is minor which is supported by findings of Rahman et al. (2004). They modelled conservative tracer transport in a dual-porosity setup using a model with Cartesian coordinates. They estimated an error of below 9% in their studies caused by neglecting the radial diffusion into the clay matrix.

Table 2 Input parameters and fitting parameters obtained for 4-Cl-An

Input parameter	Unit	Experiment		
		A	B	C
t_0	h	12.1	21.3	38.5
P_D	–	0.0012	0.0013	0.0010
a	s$^{-1/2}$	0.75×10^{-3}	0.73×10^{-3}	0.73×10^{-3}
$\lambda_{\text{4-Cl-Nb}} = \lambda_{\text{prod}}$	h^{-1}	1.60	1.47	1.45
Fitted parameter				
R_{im}	–	2.78	3.47	2.57
K_{im}	h^{-1}	0.55	0.24	0.38

Migration of the parent compound (4-Cl-Nb) yielded the first-order reaction rate which is simultaneously the production rate of the metabolite with accuracy of about 10% (Knorr et al. 2016a). Finally, in the applied model of metabolite transport, there are two fitting parameters: the first-order irreversible reaction rate constant and retardation factor due to instantaneous equilibrium reaction. The estimated instantaneous retardation factor R_{im} was found to be independent on water flow velocity. On average, a value of 2.94 ± 0.45 was found (2.78 in experiment A, 3.47 in experiment B and 2.57 in experiment C). It was lower compared to the average R_{im} for the parent compound (4.6 ± 0.7) (Knorr et al. 2016a) which is in agreement with lower log (K_{ow}) values for 4-Cl-An (1.83) than for 4-Nb-An (2.4) (Hansch et al. 1995). Difference in R_{im} may result from (i) accuracy of the measurements of the metabolite concentration, (ii) accuracy of the modelling and/or (iii) the exactness of the knowledge about the value of the diffusion coefficient in the sediment for the metabolite. However, we find the results still accurate considering the application of the simplified model and the mentioned possible inaccuracies.

Also, the first-order irreversible reaction rate K_{im} (on average 0.39 ± 0.16 h^{-1}) was found to be independent on water flow velocity. Values of 0.55, 0.24 and 0.38 h^{-1} were estimated for experiment A, B, and C, respectively (on average 0.39 ± 0.16 h^{-1}). Expecting that both parameters should be principally independent from the water velocity, accuracy was estimated from parameters found in experiment A, B and C. The accuracy was about 40 and 15% for the irreversible reaction rate and the retardation factor, respectively. Taking into account the uncertainties of all parameters and its superposition, we can estimate that the irreversible rate constant is found with the accuracy up to 80% and the retardation factor with the accuracy of about 30%. The application of more complicated models with additional parameter(s) will improve the fitting but surely will not improve the uncertainties in parameter estimation. Simultaneously, the increase of fitting parameters would reduce the possibility of yielding the unique solution.

The first-order irreversible sorption rate of 4-Cl-An can be interpreted as either degradation or irreversible sorption which cannot be distinguished in the current experiment. However, a degradation of 4-Cl-An is unlikely because of several reasons. Within the dual-porosity column, anoxic conditions would require anaerobic degradation pathways, which have not been reported in literature to date. In general, anilines are degraded by a carboxylase followed by reductase under anoxic conditions. However, the position of the Cl in 4-Cl-An prevents these reactions (Schnell et al. 1989; Schnell and Schink 1991). Another possibility is that 4-Cl-An is degraded under aerobic conditions because the effluent became aerobe once it left the column. 4-Cl-An is known to be degradable by microbes under aerobic conditions (Hongsawat and Vangnai 2011; Vangnai and Petchkroh 2007; Zeyer et al. 1985; Zhang et al. 2013). However, biodegradation of 4-Cl-An occurs only on a small extent over a larger period of time (weeks) (Bollag et al. 1978), much larger time steps compared to the time of sample preparation before analysis in this study (hours). Bollag et al. (1978) studied the adsorption and transformation of 4-Cl-An in autoclaved and nonautoclaved soil. Batch experiments indicated that after 6 weeks of incubation, only approximately 7.5% was degraded biologically. Therefore, an irreversible sorption process of 4-Cl-An is more likely. Sorption can occur either on clay minerals in the immobile water region or on the quartz sand in the mobile region. Sorption onto iron oxides which may have precipitated during the experiment can be excluded because Pizzigallo et al. (1998) found no sorption of 4-Cl-An on iron oxides at a pH of 7. The sorption onto quartz sand has not been investigated yet, but it was found to be negligible for the parent compound 4-Cl-Nb (Haderlein et al. 1996). Since the chemical structure of 4-Cl-An and 4-Cl-Nb is similar, comparable sorption characteristics towards quartz seem to be reasonable. This is further supported by the identical peak times of 4-Cl-Nb and 4-Cl-An. Bollag et al. (1978) found in batch experiments that almost 49% of 4-Cl-An was bound to the soil after 24 h. They argue that biodegradation is negligible in that period of time and that sorption occurs on organic matter rather than on clay minerals (Hsu and Bartha 1973). Kowalska and Cocke (1998) investigated the interaction of 4-Cl-An with montmorillonite. 4-Cl-An reacted with this clay mineral forming a condensation product while the reaction was dependent on the available exchangeable cations. The chemical sorption proposed by Kowalska and Cocke (1998) might be also reasonable processes explaining the decay of 4-Cl-An in dual-porosity column experiments since the applied clay consisted of 11–14% montmorillonite minerals (Compactonit 10/80, GWE p umpenboese GmbH, Germany).

The presented analytical model can be used to quantify important transport processes for compounds formed within a dual-porosity system. Since many parameters are unknown, it is useful to estimate flow and transport applying a multitracer approach. Thus, the number of fitting parameter is reduced for further reactive transport modelling. Estimated mean transit time and the dispersion parameter can be directly used. The advantage of the provided analytical solution is that diffusive mass exchange is described based on the solute's diffusion coefficient. From conservative tracer, estimated diffusion parameter can easily be adapted to properties of other compounds (Eq. 9) when knowing their diffusion coefficients. Furthermore, the solution accounts for dispersion in the mobile water region and instantaneous contaminant input. This was not the case in already existing models like the one developed by Sudicky and Frind (1984). The presented model was applied to quantify transport in porous medium in context of this study. However, the solution can be used both in porous and fractured systems because the original solution presented by Maloszewski and Zuber (1985, 1990) was developed for single fracture systems.

Conclusions

An analytical solution based on the SFDM describing transport of metabolites in dual-porosity systems is provided. The model accounts for instantaneous sorption, first-order production and first order-decay of the metabolite. Transport is described by advection and dispersion in the mobile water region. Exchange between mobile and immobile water regions is governed based on the molecular diffusion coefficient. The model was applied to quantify transport of 4-Cl-An in dual-porosity column experiments. It was shown that the number of fitting parameter can be reduced by fitting stepwise tracer, parent compound and metabolite data. Mean transit time, dispersion parameter and diffusion parameter were estimated from multi-tracer experiments. The first-order production rate was estimated from the parent compound 4-Cl-Nb. The only remaining fitting parameters to describe transport of 4-Cl-An were the first-order irreversible sorption rate and the instantaneous retardation factor. Both the retardation factor ($R_{im} = 2.94 \pm 0.45$) and first-order irreversible sorption rate ($K_{im} = 0.39 \pm 0.16 \, h^{-1}$) were found to be independent on water flow velocity. The presented analytical model helps to understand transport processes of metabolites in a dual-porosity system. It can quantify important transport processes for compounds formed in dual-porosity systems. For unique parameter identification, it has to be combined with a multi-tracer approach. This is important for a reliable prediction of contaminant fluxes. It can be applied to both porous and fractured systems to determine sorption, production and decay rates for specific contaminants.

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