Experimental and modeling analysis of coupled non-Fickian transport and sorption in natural soils

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We present experimental breakthrough curve (BTC) data and a modeling investigation of conservative and sorbing tracer transport in natural soils. By analyzing the data using the continuous time random walk (CTRW) model, we probe the traditional approach of using conservative tracer model parameters as a basis for quantifying the transport of sorbing solutes in the same domain when non-Fickian transport is present. Many known contaminants in groundwater are sorbed to the host solid porous medium, to varying extents, while being transported; this enhances the long tailing of BTCs which often already occurs because of the inherent non-Fickian nature of the transport. The CTRW framework has been shown to account very well for non-Fickian conservative (nonsorbing) transport. Here, we examine two BTC data sets in laboratory columns packed with natural soils; the first (previously analyzed by Mao and Ren (2004)) comprises transport of (conservative) bromide and (sorbing) atrazine tracers, while the second presents new data with bromide and tribromomethane (TBNPA), a key flame retardant, as a sorbing solute. TBNPA has received little attention in the past, and is shown to be sorbed onto Bet Dagan soil in a nonlinear manner. We find that the transport behavior of bromide is non-Fickian in all cases, which is caused by the heterogeneity of the soil. Comparative model analysis of the non-Fickian BTCs of the conservative, and sorbing tracers and examination of the fitting parameters, exemplify the coupling between transport and adsorption/desorption processes. The difference in transport parameters used to match the conservative and sorbing data sets shows that conservative tracer parameters (average velocity and dispersion coefficient) are not valid for the transport of reactive tracers.

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CTRW
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1. Introduction

It has been recognized widely that chemical transport in porous media often exhibits non-Fickian behavior, as low velocity regions in heterogeneous media strongly affect the transport (e.g., Berkowitz and Scher, 1998; Eggleston and Rojstaczer, 1998; Rhodes et al., 2008). Non-Fickian transport can be observed, for example, in the form of breakthrough curves (BTCs) that deviate from the functional form predicted by the advection–dispersion equation (ADE), typically in long tailing of BTCs.

Adsorption/desorption processes may lead to further enhancement of the asymmetry of BTCs. Traditionally, transport of sorbing solutes is modeled by assuming underlying Fickian transport (given by the ADE), and the long tailing of the BTC is attributed solely to adsorption effects (e.g., Gaber et al., 1995; Hatano and Hatano, 1998; Mao and Ren, 2004; Nkedi-Kizza et al., 1989). In these cases, the transport parameters are calibrated by a tracer test, where the fluid velocity is applied, and a fit to the ADE provides the dispersion coefficient. Sorption is accounted for by adding a sink term to the ADE, which describes the mass loss of solute tracer. This form can be converted to an ADE with a retardation factor that has the effect of decreasing the magnitude of the advective and dispersive components of transport. Information on sorption kinetics or adsorption isotherms obtained from batch experiments is used to construct
a functional relation between the adsorbed concentration and the resident concentration, which defines the retardation factor. In the case where a linear adsorption isotherm is valid, the retardation factor incorporates the distribution coefficient $K_d$.

Models that apply various versions of an ADE with a retardation coefficient often fail to accurately describe BTC data, especially the long tails (see, e.g., Fig. 2 in Hatano and Hatano, 1998, and Fig. 3 in Cortis et al., 2006). In such an approach, the underlying non-Fickian transport is not accounted for. Instead, the Fickian transport parameters $v$ (fluid velocity) and $D$ (tracer dispersion coefficient) are further employed to model transport of the reactive solute. In addition, parameters obtained in batch experiments may not be relevant for further application in transport experiments. This is due to several possible reasons: (i) the different timescales involved, which indicate whether the system has reached equilibrium (Maraqa et al., 1999; Nkedi-Kizza et al., 1989; Zhang and Selim, 2006), (ii) the different degrees of solute mixing in the column, which affect transfer rates, and (iii) different mass ratios for chemical saturation. The inadequacy of employing parameters a priori from batch mode to transport experiments can be explained, at least partly, by the link between reaction parameters and the flow rate under kinetic conditions (see for example Pang et al., 2002, Zhang et al., 2008 and references therein).

The significance of the coupling between transport and reaction processes arises from recent investigations. In a theoretical study of a reaction–diffusion process, it was shown that the effective diffusivity depends on the homogeneous reaction rate (Valdes-Parada and Alvarez-Ramirez, 2010). Using a particle tracking approach, Edery et al. (2009, 2010) illustrate the feedback mechanism of the pore velocity distribution and the reaction rate in a bimolecular reaction; after an initial phase of reaction, the reaction rate is influenced by fluctuations of the underlying velocity field. The reaction modifies the effective dispersion coefficient as a result of the chemical gradients which are created. Traditional models that employ the ADE with the addition of reaction (by introducing an external retardation parameter), assume a homogeneous medium in two aspects: homogeneous porous medium that dictates Fickian transport, and homogeneous mixing of solute, which often overestimates the overall reaction rate. In this way, the velocity field and dispersion are not linked to the reaction dynamics, and can be modeled as separate processes which occur side by side. Recently, Porta et al. (2012) demonstrate theoretically the coupling between transport and reaction properties.

The CTRW framework has been proven to be a highly effective tool to describe non-Fickian behavior of particles flowing through porous media (Berkowitz et al., 2006). In CTRW, transport is viewed as a sequence of particle transitions with displacement $s$ and time $t$ with a probability density $\psi(s,t)$. One of the main advantages offered by CTRW lies in its ability to describe advective–dispersive transport in the systems where less frequent (or even very rare) statistical events have a considerable impact on the overall non-Fickian behavior. Several theoretical advances shed light on the emergence of anomalous transport from various simulated heterogeneous velocity fields (e.g., Le Borgne et al., 2008; Willmann et al., 2008). When mass exchange such as adsorption/desorption processes takes place during solute transport, non-Fickian behavior (exhibited by long tailing of BTCs) can be caused both by heterogeneities of the medium (which lead to solutes encountering a broad range of local velocities) and by retardation of solutes by sorption. In cases where the timescales of transport and sorption processes overlap, the two processes can be merged into an effective cause for non-Fickian transport (Deng et al., 2008; Li and Ren, 2009). The unresolved heterogeneity of the porous medium affects not only the transport process (apparent in the conservative tracer BTC tailing), but also the degree of mixing of solute which further influences the sorption reaction (Edery et al., 2009, 2010). Moreover, Dentz and Castro (2009) and Dentz and Bolster (2010) showed numerically that a random retardation field can be upscaled exactly to a CTRW.

Because the effect on transport has been modeled previously using CTRW successfully, we employ the same approach to describe ‘unresolved chemical heterogeneity’ that is added to the system (which cannot be quantified by batch experiments). We first apply the CTRW model to examine the interacting transport and sorption mechanisms, re-analyzing data from an experiment that measured BTCs for simultaneous transport of bromide, a conservative (non-sorbing) tracer, and atrazine, a sorbing chemical species (Mao and Ren, 2004). We then present an independent data set, using a separate solute and soil with different transport and sorption properties, and demonstrate the validity of the CTRW analysis. We hypothesize that the processes of transport and sorption cannot be separated conceptually, and should be modeled in a ‘lumped’ manner. We study the organic compound tribromoneopentyl alcohol (TBNPA). This compound, which is known to be carcinogenic (Dunnick et al., 1997) and has a relatively strong resistance to biodegradation (Ezra et al., 2006), is used for synthesis of high molecular-weight flame retardants and as a reactive flame retardant for polyurethanes. Together with its high solubility in water, TBNPA poses a serious threat to groundwater quality. We perform TBNPA batch and laboratory column experiments with Bet Dagan (Israel) soil and bromide as a conservative tracer in a similar manner to that of Mao and Ren (2004).

2. CTRW model

In the CTRW framework, a master equation conserving solute mass can be developed into a transport equation in partial differential equation (pde) form. For a concise derivation starting from a simple random walk and leading to the transport equation, see Berkowitz et al. (2006). By assuming the decoupled form $\psi(s,t) = \psi(t)\rho(s)$ we can write the transport equation in Laplace space, $\mathcal{L}$ (denoted by $\mathcal{L}$ and Laplace variable $\mu$) as

$$\mathcal{L}(t) = \left[\nu_\psi \nabla \mathcal{L}(s) - D_\psi \cdot \nabla \nabla \mathcal{L}(s)\right]$$

where $\nu_\psi = \frac{1}{t} \int p(s) ds$ is the tracer transport velocity (which may be distinct from the fluid velocity), $D_\psi = \frac{1}{t} \int p(s) s^2 ds$ is a generalized dispersion tensor, $M(u) = t_1 u \frac{\phi(u)}{1-\phi(u)}$ is a ‘memory’ function, $t_1$ is characteristic transition time and $c_0(s)$ is the initial concentration (Berkowitz et al., 2006 and references therein).
The probability density function (pdf) $\psi(t) = \mathcal{L}^{-1}\tilde{\psi}(u)$ is defined as the probability rate for a transition time $t$ between sites. Its determination lies at the heart of the CTRW as it determines the nature of the transport. The truncated power law (TPL) form of $\psi(t)$ has been applied successfully to a wide range of physical scenarios (Berkowitz et al., 2006). The ‘cut-off’ of the power law allows a transition from anomalous behavior to Fickian behavior at longer times. The TPL form can be written as $\psi(t) = \frac{N}{\Gamma(\beta)} \left( \frac{\Gamma(\beta)}{\Gamma(\beta + 1)} \right)^{\frac{1}{\beta}} t^{-\frac{1}{\beta}} e^{-\left( \frac{\Gamma(\beta)}{\Gamma(\beta + 1)} \right) t}$ is a normalization factor, $\beta$ is a measure of the dispersion, $t_N$ is a 'cut-off' time ($> t_1$) and $\Gamma(\alpha, x)$ is the incomplete gamma function. Note that $\psi(t) = \left( \frac{1}{\gamma} \right)^{-1-\beta}$ for $t_1 \ll t \ll t_2$, and decreases exponentially $\psi(t) = e^{-\beta t}$ for $t > t_2$. Fickian transport occurs for $\beta > 2$, while the transport is increasingly dispersive for decreasing $\beta$.

The 1D CTRW transport equation can be transformed into dimensionless form, by normalizing the time and length dimensions by characteristic time and length scales of the problem, e.g., by $t_N$ and $D_0$, respectively, so that the dimensionless variables (denoted by *) are

$$u^* = t_N u, \quad x^* = \frac{D_0}{v} x.$$

We choose these characteristic time and length scales in order to include dynamical properties in the problem, rather than external, structural properties (such as the column length or grain size). This allows a universal approach for studying the dynamics that construct the BTC. The resulting non-dimensional transport equation becomes

$$u^* \frac{\partial c^*(x^*, u^*)}{\partial x^*} - c_0(x^*) = -\bar{\delta} M(u^*) \left[ \frac{\partial^2 c^*(x^*, u^*)}{\partial x^2} - \frac{\partial c^*(x^*, u^*)}{\partial x^*} \right]$$

where $\bar{\delta} = t_N \frac{v}{D_0}$ is a non-dimensional parameter. Converting the boundary condition in the same manner to be $c^*(0, u^*) - \frac{\partial c^*(0, u^*)}{\partial x^*} = \frac{1}{M(u^*)}$ and $\frac{\partial c^*(x^* = \gamma, u^*)}{\partial x^*} = 0$, yields a different analytical solution in Laplace space which can be then converted numerically to the time domain. The parameter $\bar{\delta}$ makes the use of both $v_0$ and $D_0$ unnecessary, and thus facilitates the curve fitting procedure by reducing the number of parameters in the problem by one. Because parameters of the experimental set up or parameters from batch experiments are not always relevant for describing transport (see Section 1 and 7), this approach may serve as a first step toward implementing parameters which include an inherent combination of dynamic properties that directly affect the BTC.

Figs. 1 and 2 present the solutions of the dimensionless flux-averaged and resident concentrations, respectively, when $\bar{\delta}$ is varied. These figures indicate that the breakthrough becomes increasingly delayed as $\bar{\delta}$ decreases. Because the parameter $t_N$ affects the BTC tailing (in addition to the effect of the $\beta$ parameter), varying $\bar{\delta}$ which includes $t_N$ modifies these tailing properties as well.

**3. Materials and methods**

**3.1. Materials**

TNBA (97%) was supplied from Dead Sea Bromine Group, KBr (Sigma 99.9%), Bet Dagan (Israel) soil, sandy loam Mediterranean red soil (Rhodoxeralf), was taken from the upper 10 cm layer and sieved by 60 mesh sieve, i.e., maximum grain size was 250 μm. A fraction of 8.9% of the dry soil mass is smaller than 125 μm and 6.3% is smaller than 63 μm. The soil is characterized by 16.2% clay, 6.3% silt, 77.5% sand and 1.2% organic carbon. Bet Dagan soil porosity when packed in the saturated column was 0.40. Double-distilled water (DDW) employed in the experiments had 18.2 MΩ cm resistivity.

**3.2. Batch experiments**

Batch experiments were carried out (in triplicates), with 10 g Bet Dagan soil and 15 mL TBNPA solutions with seven
initial concentrations (100, 50, 10, 5, 1, 0.5 and 0.1 ppm) at pH 7, in 40 mL glass vials with teflon caps. Control samples were prepared with soil and DDW only, to check for natural presence of TBNPA in soil and the highest initial concentration with no soil, to check possible adsorption to the reaction vessels. Samples were shaken for 72 h at 160 rpm, then centrifuged and filtered through 0.22 μm syringe filters (Millex Millipore made from PVDF). The sample solutions were extracted by half their volume of toluene, from which 1 μL was injected into a gas chromatograph (GC) using an autosampler. The reproducibility error of the peak area was <3%.

3.3. Column experiments

Laboratory-scale transport experiments were carried out in a vertically placed column packed with soil, into which solution was pumped with a HPLC pump (Prep 100 Cole Palmer) from the column bottom to its outlet at the top, where samples were collected automatically using a fraction collector (ISCO Foxy Jr.). To saturate the soil and equilibrate it with the solution, DDW was pumped into the column overnight with a 0.5 mL min⁻¹ flow rate. To prevent adsorption of the organic solute onto the solid materials, an aluminum column and teflon tubing were used. Column dimensions were 20.0 cm in length and have 1.55 cm internal radius. Input solution to the column was switched between DDW, and a solution of the conservative or sorbing tracers, using a 3-way valve. The transport experiments were performed with two flow rates, 1.8 mL min⁻¹ and 6.0 mL min⁻¹, both with bromide and with TBNPA, and were repeated at least twice. The reproducibility of the measurements was well within the variability range of natural soils in repacked columns (Lewis and Sjöström, 2010).

3.4. TBNPA analysis

Analysis of TBNPA was done using a GC/ECD (Agilent 5890) equipped with DB-VRX (30 m length, 0.32 mm inner diameter, 1.8 μm film thickness) capillary column. The GC carrier gas was helium, at a flow rate of 1 mL min⁻¹. The GC temperature program was as follows: 100 °C for 1 min; temperature ramp of 15 °C min⁻¹ to 250 °C; 250 °C for 3 min.

3.5. Bromide analysis

High-performance liquid chromatography (HPLC) system (Waters 1525 binary HPLC pump) equipped with an Alltech conductivity detector. Model 650 was used to analyze Br⁻ concentrations. The anion separation was done on an Alltech Alsepp Anion 7u analytical column (100 mm × 4.6 mm 1D). The mobile phase was 4 mM hydroxybenzoic acid in DDW, at pH 7.5 with LiOH, with flow rate 1 mL min⁻¹.


4.1. Data

Mao and Ren (2004) performed batch and column experiments to examine simultaneous transport of a conservative tracer (bromide) and a sorbing tracer (atrazine) in Changping Shahe (China) soil. The column experiment was repeated in two columns, using a square input pulse, and BTCs were recorded for both solutes at the outlet of each column. Full details regarding the experimental set-up are given in Mao and Ren (2004).

A large degree of variability between the two columns can be observed (Mao and Ren, 2004), even though the experimental conditions were essentially identical (the second experiment was performed in a column that was 1% narrower, with a 2% larger flow velocity). The variation between the two BTCs, in the long tail region between 2.5 and 3.5 pore volumes (not shown), can be characterized by the average difference between the relative concentrations recorded in the two experiments in this region. This value is calculated to be 0.0033 (dimensionless) and serves as the error bar in Fig. 3. This variation may be caused by natural variation in the soil material, and/or by the heterogeneity introduced during packing of the two columns (Bromly and Hinz, 2004). Note also that, while not discussed in Mao and Ren (2004), (i) air bubbles which affect the flow field may have been created during the 36 h long experiment; and (ii) the reported detection limit of the HPLC system is 4 ppb for atrazine, so that measurement of the low concentrations appearing in the early and late times of the BTC can be detected only by sample extraction techniques (which can increase the degree of error).

Mao and Ren (2004) also carried out batch experiments to study atrazine sorption on Changping Shahe soil. The equilibrium sorption isotherm for atrazine was described by a linear Freundlich equation, and its Kᵣ was used as a parameter for the transport model analyses.
4.2. Atrazine transport and sorption in soil

Mao and Ren (2004) inferred Fickian transport behavior by examination of the bromide BTC data plotted on a linear concentration scale. As a consequence, they attributed the tailing observed in the BTC of atrazine exclusively to sorption effects. However, plotting the concentration on a logarithmic scale allows closer examination of the long-time behavior.

Fig. 3 presents the bromide and the atrazine BTCs from an experiment of Mao and Ren (2004). In this figure, the bromide BTC clearly exhibits a long tail. Beyond 1.4 pore volumes (= 870 min) the bromide BTC displays a tail of concentration higher than that characterized by the ADE. Thus in this column, transport of conservative species is seen to be non-Fickian. We find that the bromide BTC can be described by the TPL form of CTRW (solid gray curve in Fig. 3); here, the tracer velocity \( v \) is larger than the measured value of fluid velocity \( v \), and \( D \), the generalized dispersion, is smaller than the estimated value of \( D \), both by approximately 30%. The fitted value of \( \beta = 1.64 \) is indicative of non-Fickian transport. It can therefore be hypothesized that a part of the long tailing of any sorbing tracer in the same experimental set-up may be attributed to the inherent heterogeneities of the porous medium, in addition to the obvious effect of sorption.

The measured atrazine BTC data are presented in Fig. 3, with error bars computed from the average variation observed between the two experiments carried out in Mao and Ren (2004). Relative to the bromide data, the concentration peak is delayed to ~1.5 pore volumes (=930 min) and \( t_1 = 10^{0.5} \) min, which obviously indicates transport regime which is more anomalous, compared to the conservative case, but also a longer characteristic transition time which incorporates the sorption retardation effect.

5. Results and analysis

5.1. TBNPA sorption in batch experiments

A batch experiment was carried out to study the equilibrium sorption isotherm in a well-mixed reactor. Fig. 4 shows the adsorption isotherm obtained as adsorbed mass, \( q_{eq} \) (calculated from the measured concentrations, soil mass and fluid volumes), versus concentration in solution, \( c_{eq} \), at equilibrium. The data are fit to the empirical nonlinear Freundlich curve, \( q_{eq} = K_F c_{eq}^n \) with \( R^2 = 0.988 \), where \( K_F = 1.604 \), \( n = 1.1038 \); \( K_F \) and \( n \) are indicators of adsorption capacity and adsorption intensity, respectively. In this case adsorption is favorable, because \( n > 1 \). We note that because \( q_{eq} \) is calculated from \( c_{eq} \), the two variables are not independent, and therefore the value of \( R^2 \) serves only as an indicator of fitting quality (e.g., Asuero et al., 2006).

The units of \( K_F \) are \( \text{mg/kg} \), so that comparison to \( K_F \) values of different materials (with different \( n \) values), or specifically to the \( K_F \) value for atrazine (equivalent to \( K_F \) with \( n = 1 \), i.e., the linear isotherm) obtained in Mao and Ren (2004) is not straightforward. Therefore, the linear atrazine isotherm is plotted in Fig. 4 for reference, for the range of the atrazine data in Mao and Ren (2004). The comparison shows that the fraction of adsorbed TBNPA is larger than that of atrazine, with an increasing adsorbed fraction with increasing solute concentration (note that this is a logarithmic plot).

5.2. Bromide transport in soil

Bromide BTCs for the flowrates 1.8 mL min\(^{-1}\) and 6 mL min\(^{-1}\) are presented in Figs. 5 and 6, respectively. In both cases a tailing of bromide concentration developed after two pore volumes. An ADE fit to these data, with the measured fluid velocity, does not describe this tailing. A fit of the CTRW model in Fig. 5 demonstrates weak non-Fickian behavior, with \( \beta = 1.96 \) (close to 2, which represents Fickian transport). The average tracer velocity, \( \psi_F \), is larger than the measured fluid velocity, which is consistent with the slightly earlier breakthrough than that predicted by the ADE.

The model fit of the experimental data with the faster flowrate (Fig. 6) points towards transport behavior that is more anomalous, according to the fitting parameters \( \beta = 1.8 \) and the larger time range of power-law solute transitions (\( t_2 \) is smaller and \( t_2 \) is larger than in Fig. 5). The average tracer velocity in this case is 25% larger than the fluid velocity. It should be noted that differences in the transport behavior occur when the flowrate alone is changed. Thus, in the same experimental set up, with same structural heterogeneity of the soil, a shorter residence time causes transport to be more anomalous, as reported in Cortis et al. (2004).
5.3. TBNPA transport and sorption in soil

The experimental results of TBNPA transport are presented in Figs. 7 and 8, corresponding to flowrates of 1.8 mL min$^{-1}$ and 6 mL min$^{-1}$, respectively. In the first experiment, the input function is a pulse of concentration 100 ppm and duration 34.44 min (~1 pore volume). The CTRW model fit with a TPL transition rate pdf captures the BTC tailing, and indicates the existence of non-Fickian transport with $\beta = 1.56$. Compared to the bromide BTC with the same flowrate (Fig. 5), the first arrival and peak solute concentration appear ~1 pore volume later than in the conservative tracer case. In addition, the TBNPA BTC exhibits a more prominent tail. Both the delay of the peak concentration and the tailing features are influenced by the additional process of adsorption/desorption of TBNPA onto/from the soil, which enhances the non-Fickian transport present also in the conservative tracer results under the same experimental conditions. However, compared to its conservative counterpart, $t_1$ is larger, which reduces the non-Fickian transition time range of the TPL pdf.

In the second TBNPA experiment (Fig. 8), the input function is a pulse of concentration 100 ppm and duration 10.33 min (~1 pore volume). Similarly to the slower flowrate experiment, the TBNPA BTC shows delayed breakthrough compared to the conservative BTC under the same experimental conditions (Fig. 6), both at the peak concentration and its tail. The CTRW TPL model matches this non-Fickian transport, with a lower $\beta$ and $v_\psi$ and a larger $t_1$ compared to the corresponding conservative transport.

Fig. 5. Experimental BTC data of bromide of two experiments, the inlet concentration in one BTC is $c_0 = 200$ ppm (squares) and 600 ppm in the second BTC (circles) with flow rate of 1.8 mL min$^{-1}$. Pulse duration is 30 min. Model fits are plotted: ADE fit (dotted line) with the parameters $v = 0.596$ cm min$^{-1}$ $D = 0.12$ cm$^2$ min$^{-1}$ and TPL fit (solid line) with the parameters $v_\psi = 0.64$ cm min$^{-1}$, $D_\psi = 0.12$ cm$^2$ min$^{-1}$, $\beta = 1.96$, $t_1 = 10^{-2}$ min, and $t_2 = 10^6$ min.

Fig. 6. Experimental BTC data of bromide of two replicate experiments (circles and squares) with inlet concentration of 600 ppm, flow rate of 6 mL min$^{-1}$ and pulse duration of 9 min. Model fits are plotted: ADE fit (dotted line) with the parameters $v = 1.988$ cm min$^{-1}$ $D = 0.24$ cm$^2$ min$^{-1}$, TPL fit (solid line) with the parameters $v_\psi = 2.5$ cm min$^{-1}$, $D_\psi = 0.24$ cm$^2$ min$^{-1}$, $\beta = 1.8$, $t_1 = 10^{-2.9}$ min, and $t_2 = 10^6$ min.

Fig. 7. Experimental BTC data of TBNPA from two replicates (squares and stars) with inlet concentration of 100 ppm, flow rate of 1.8 mL min$^{-1}$ and pulse duration of 34.44 min. A TPL model fit of TBNPA data is plotted (solid line) with the parameters $v_\psi = 0.44$ cm min$^{-1}$, $D_\psi = 4 \times 10^{-2}$ cm$^2$ min$^{-1}$, $\beta = 1.56$, $t_1 = 10^{-0.7}$ min, and $t_2 = 10^6$ min.

Fig. 8. Experimental BTC data of TBNPA from three replicates (circles, squares and stars) with inlet concentration of 100 ppm, flow rate of 6 mL min$^{-1}$ and pulse duration of 10.33 min. A TPL model fit of TBNPA data is plotted (solid line) with the parameters $v_\psi = 1.7$ cm min$^{-1}$, $D_\psi = 0.32$ cm$^2$ min$^{-1}$, $\beta = 1.45$, $t_1 = 10^{-1.9}$ min, and $t_2 = 10^6$ min.
are often correlated to sorption rates (Haggerty et al., 2004). Shape significantly. Indeed, characteristic advection time scales time, interplay between these processes can affect the BTC time regime that is comparable to the typical mass exchange materials). As a consequence, as the residence time is reduced to a velocities (for the same experimental set up and the same ma-

truncates possible solute sampling of long mass exchange

D

\[ \psi \]

\[ v \psi /v \]

\[ D_{v/D} \]

\[ \delta \]

\[ s \] [μm]

Similar to the conservative tracer experiment, comparison be-

tween the two TBNPA experiments demonstrates that a higher flowrate results in transport that is more anomalous. This is indicated by the lower \( \beta \) and wider non-Fickian time range in the faster flowrate case (Fig. 8) compared to the slower flowrate condition (Fig. 7). The importance of solute residence time demonstrates the dynamic nature of the controlling parameters, not only when non-Fickian transport is caused by heterogeneity (Figs. 5 and 6), but also when the additional controlling transport mechanism is sorption. A faster flowrate results in a larger tail of the sorbing solute BTC. Whether this is a result of the underlying non-Fickian transport (as concluded from the conservative tracer analysis) or a result of the sorption process alone is not well-defined. Moreover, a higher flowrate causes greater solute dispersion, as indicated by the larger \( D_{v/D} \). A shorter residence time truncates possible solute sampling of long mass exchange rates, which results in different fitted rates for different flow velocities (for the same experimental set up and the same materials). As a consequence, as the residence time is reduced to a time regime that is comparable to the typical mass exchange time, interplay between these processes can affect the BTC shape significantly. Indeed, characteristic advection time scales are often correlated to sorption rates (Haggerty et al., 2004).

It is evident from the fitting parameter values that the con-

servative tracer values of average velocity, \( v_{t} \), and generalized dispersion, \( D_{v/D} \), cannot be applied further for the analysis of the sorbing tracers. For both flowrates, the conservative tracer velocity is greater than the sorbing tracer velocity by ~30%.

### Table 1

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<th>Sorbing</th>
<th>TBNPA slow flow rate</th>
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6. **Discussion**

Conservative transport in previously published data and in our experimental set-up (for two flowrates) demonstrates persistent anomalous behavior. Transport of sorbing tracers under the same experimental conditions amplifies further the non-Fickian nature of transport, in the form of delayed peak concentration and longer tailing, which points to relatively fast sorption compared to transport time scales (Bijelic et al., 2011). We have analyzed both conservative and sorbing tracer BTC data successfully using the CTRW model with a TPL pdf.

Table 1 summarizes the CTRW TPL parameters that fit the data. Comparing the CTRW TPL parameters of the sorbing tracer to the parameters of the conservative tracer of the same experimental conditions reveals that when the conservative tracer behavior is already non-Fickian, a good description of the sorbing tracer transport in the same experimental set up requires a change not only to the values of \( \beta \) and \( t_{1} \) of the TPL \( \psi(t) \) function, but also to the underlying \( v_{t} \) and \( D_{v/D} \) parameter values. A closer look at the fitting parameters reveals a negative correlation be-

\[ \beta \]

\[ v_{t}/v \]

\[ D_{v/D} \]

\[ \delta \]

\[ s \] [μm]

Fig. 9. Correlation between \( \beta \) and \( v_{t}/v \) for the conservative and sorbing data fits. The arrows point to conservative-sorbing coupled data set of the same experimental conditions (column set up and flow rate): a represents the data of Mao and Ren (2004), b represents the new data with the fast flow rate, and c represents the new data for the slow flow rate.
one can expect that to describe the transport of a sorbing tracer, both $\beta$ and $v_0$ of its conservative counterpart should be reduced. In addition, $t_0$ of a sorbing tracer is larger than the conservative equivalent, as the effective transition rate is slower due to the retardation of solute. The parameters $D_0$ and $t_0$ are seen to have a negligible influence. One can also calculate the characteristic transition length $s = v_0 \cdot t_1$ (Table 1). The characteristic transition length of a sorbing tracer is larger by approximately an order of magnitude compared to its conservative counterpart in the same experimental set up, which is caused by the longer characteristic transition time ($t_1$) in the sorption scenario. When switching to a faster flow rate, the transition length is reduced for both conservative and sorbing solutes, as the increase in the tracer velocity does not compensate for the large decrease in the median transition time. Relating $s$ to the soil grain size is not obvious, because it varies over an order of magnitude for a given porous medium. The range of $s$ values for Bet Dagan soil (Section 3.1) lies in the range of the grain size to a small aggregate of a few grains.

Another development to the CTRW model (Berkowitz et al., 2008) involves two distinct time scales for solute transport. These arise from the different mechanisms of ‘pure’, non-reactive, transport (which is most often non-Fickian), and a mass exchange mechanism, such as sorption. This “two-scale” model contains an effective memory function that is a convolution of two memory functions, one for each of the above-mentioned mechanisms. An extensive analysis of the atrazine and TBNPA data using the two-scale CTRW model (not shown) shows no improvement of the fitting quality, compared to the analysis presented in Fig. 3. However, two important notes regarding this analysis should be emphasized. First, the interpretation of the relevant model inherent parameters is essentially different in the two cases. In the two-scale model, one set of parameters can be attributed to the transport alone, while a second set of parameters relates to the sorption mechanism. In contrast, in the analysis presented here, the two processes cannot be distinguished in terms of their influence on the overall non-Fickian (tailing) behavior. In this context although there are fewer model parameters and the model has a simpler form, we lose information when only one time scale is incorporated. Second, the inability to determine the transport parameters independently, based on the conservative data (bromide), and use them to quantify the transport of a sorbing tracer (atrazine or TBNPA), essentially changes the nature of the underlying non-Fickian transport and points to a possible interplay between the processes involved. Because the time scales of the non-Fickian transport and the sorption process overlap in the atrazine and TBNPA transport data, and are not well separated (not shown), a ‘lumped’ analysis such as presented by Deng et al. (2008) and Li and Ren (2009) is sufficient, as it represents the complex combined effect of the two processes in the simplest form.

7. Concluding remarks

We have developed new measurement protocols for TBNPA and investigated this little studied but critical environmental compound. The experimental and modeling study presented here offers a general approach to quantification of transport of such organic compounds in soils. Our results validate the accuracy of the concentration measurements over more than three orders of magnitude, which enables experiments that record the long breakthrough tail accurately. Batch and column experiments indicate that TBNPA is sorbed onto Bet Dagan soil in a weakly nonlinear manner, quantified by the nonlinear Freundlich isotherm: $c_{eq} = 1.604c^{0.06}$. This is unlike the linear sorption behavior reported in Mao and Ren (2004) for atrazine, although for a narrower concentration range.

Traditionally, transport of sorbing solutes is calibrated by the parameters of a conservative tracer in the same experimental set up, with the addition of sorption parameters for the specific sorbing solute and porous material, obtained in batch experiments, under equilibrium conditions. The approach of applying parameters from batch experiments onto non-equilibrium transport experiments has been questioned previously (Nkedi-Kizza et al., 1989). We further emphasize the irrelevance of parameters obtained in batch, because the transport parameters are mostly flow rate-related. In a similar manner, unresolved heterogeneities that affect the transport (observed in the form of concentration tailing of conservative tracers), are taken into account within the CTRW framework. Transport of sorbing tracers introduces the interaction between the unresolved transport-related heterogeneity and unresolved chemical (sorptive) heterogeneity. We show that in general it is not possible to separate transport and sorption into different sets of independently measured/fit parameters, as has been the approach used for traditional advection–dispersion–reaction equation methods. In specific cases where transport is slow (e.g., purely diffusive) and the sorption reaction is fast, a traditional modeling approach (based on independent sorption parameters from batch experiments) may apply. However, in general cases, the CTRW model analysis presented here demonstrates the complex relation between the conservative and sorbing model parameters and questions the relevance of a simple ‘calibration’ by the conservative parameters.

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