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Journal of Contaminant Hydrology 39 (1999) 7–34

JOURNAL OF
Contaminant
Hydrology

Solute transport analysis of bromide, uranin and LiCl using breakthrough curves from aquifer sediment

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Received 27 August 1998; received in revised form 25 February 1999; accepted 19 March 1999

Abstract

The transport behavior of lithium, uranin, bromide and chloride was studied in column experiments using sediment from an unconfined aquifer at the Krauthausen test site. Sorption isotherms of uranin, bromide and chloride were determined in batch experiments. In addition, a sorption/desorption isotherm of uranin was determined. Inverse parameter estimation and asymptotic analysis of solute transport processes were used to interpret measured BTCs. The log transformed BTCs of bromide and chloride showed a linear decrease of the tailing part with time. Depending on the shape of the tail in the BTCs, a CDE with retardation or a mobile/immobile model was adjusted successfully. Measured uranin BTCs were described using either the CDE with hysteretic Freundlich sorption or the CDE with linear kinetic sorption. In addition, one of the measured uranin BTCs provided evidence for the presence of nonlinear nonequilibrium sorption. The discrimination and identification of the different types of sorption processes was based to a large extent on asymptotic analysis. However, in a few experiments asymptotic analysis did not provide information on the sorption process because the tailing concentrations fell below the detection limit before convergence to one of the asymptotic solutions could be observed. For none of these cases, the models analyzed in this work were able to describe the complete BTCs (including the tail). For two BTCs showing sorption hysteresis, the observed concentrations could be predicted using data from independent measurements almost without parameter fitting. Only a slight modification of the distribution coefficient was needed in one case. Lithium transport could be described either by Freundlich sorption or linear kinetic sorption. Field BTCs of uranin showed a qualitatively similar behavior as the BTCs observed in column experiments. Evaluation of the

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PII: S0169-7722(99)00033-9

slope of log–log transformed field BTCs suggested that uranin sorption may be described by a nonlinear nonequilibrium sorption or hysteretic Freundlich sorption model.

Keywords: Nonlinear sorption; Breakthrough curves; Lithium transport; Uranin transport; Batch experiments; Asymptotic analysis

1. Introduction

Characterization of solute transport in the unsaturated and saturated zone is an important element in the risk assessment of contaminants in soils and groundwater. An understanding of partitioning processes between the solid and the liquid phase plays an important role in quantifying the mass of solute available for transport. One of the major problems, however, is the identification of the underlying mechanisms and the estimation of the parameters in mathematical models describing these solid–fluid interactions. In addition, the identification of these mechanisms is obscured by the natural heterogeneity of soil and aquifer systems in terms of physical and chemical properties (Roberts et al., 1986; Thorbjarnarson and MacKay, 1994).

The classical approach for estimating parameters in transport models is to fit these models to BTCs observed in column and field experiments by minimizing a sum of squares function (Jury and Sposito, 1985). The nature of this function is in general different depending on whether ordinary least squares, weighted least squares or e.g., maximum likelihood estimation is used (Beck and Kenneth, 1977). Most frequently, parameter estimation from BTCs experiments is based on the method of ordinary least squares estimation (Parker and van Genuchten, 1984). Different minimization algorithms are used in order to obtain the minimum of the least squares function. The main disadvantages of this approach are the non-uniques of estimates, the convergence of the algorithm to a local rather than the global minimum and the ill-conditioned nature of the inverse problems leading to large perturbations on the parameter estimates. The final choice of transport models using inverse estimation methods is based on statistical criteria such as the coefficient of determination or the value of the sum of squares function (Ellsworth et al., 1996; Chen and Wagenet, 1997; Liwang and Selim, 1997). In most of these analyses no qualitative or quantitative criteria based on underlying physical and chemical processes were involved in evaluating the appropriateness of the model. One of the earliest attempts to derive transport parameters from BTCs without inverse modelling was discussed by Passioura and Rose (1971) and Rose and Passioura (1971). They presented a direct method to determine the dispersion coefficient in column experiments from the slope of the log transformed pore volume vs. the normally transformed exit concentrations of a BTC of a nonreactive solute.

In this paper we will show how asymptotic analysis may contribute to a better characterization of transport and sorption processes leading to a specific transport behavior. In addition asymptotic analysis provides equations which can be used to calculate relations between parameters or even some of the parameters themselves thereby reducing the parameter space. Combined with inverse estimation methods, asymptotic analysis provides an additional tool to evaluate and interpret BTCs.

This work was motivated by the large scale tracer experiments conducted in an unconfined aquifer at the Krauthausen field site (Vereecken et al., 1998a). The objective of the present paper is to provide a better understanding of the local scale processes involved during the transport of uranin and LiCl.

In a first part of the paper we will give a brief description of the theory involved in asymptotic analysis of equilibrium and nonequilibrium processes. In Section 3, the column and batch experiments with the tracer substances bromide, chloride, lithium and uranin are presented. This section is followed by applying asymptotic analysis and inverse estimation methods to the measured BTCs. In Section 5, conclusions are presented.

2. Theory

In the analysis of non-reactive solute transport at local scale (e.g., column experiments), the concentration evolution in the solute phase is assumed to be governed by

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} - \frac{\rho}{\theta}\frac{\partial s}{\partial t} \tag{1}$$

where c is the concentration in the liquid phase [M L^{-3}], s is the mass fraction sorbed to the sediment [M M^{-1}], θ is the porosity [M^3 M^{-3}], ρ the bulk density of the sediment [M L^{-3}], v is the mean pore velocity ($v = U/\theta$, with U the Darcian velocity) [M T^{-1}] and D the dispersion coefficient [M^2 T^{-1}]. Depending on the type of sorption occuring in the sediment, different mathematical formulations of the term $\frac{\partial s}{\partial t}$ can be given. In general a distinction is made between equilibrium and nonequilibrium models (Fetter, 1993). Assuming equilibrium conditions, the relation between c and s may be described by sorption isotherms. In case of linear equilibrium, Henry's isotherm is used:

$$s = k_d c, \tag{2}$$

where k_d is equal to the distribution coefficient.

Introducing Eq. (2) in Eq. (1), we obtain:

$$\left(1 + \frac{\rho}{\theta}k_d\right)\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} \tag{3}$$

where the term $(1 + \frac{\rho}{\theta}k_d)$ is defined as retardation coefficient R. Many substances are known to undergo nonlinear equilibrium sorption which is described by e.g., Langmuir or Freundlich isotherm (Senesi et al., 1994; Meyer-Windel and Lennartz, 1995; Xue et al., 1995, Ajwa and Tabatabai, 1997):

$$s = \frac{k_1 c}{1 + k_2 c} \quad \text{(Langmuir)}$$

$$s = kc^n \quad \text{(Freundlich)}, \tag{4}$$

where k, k_1, k_2 and n are parameters which need to be determined from sorption or solute transport experiments. Substituting Eq. (4) in Eq. (1) gives a transport equation with a time or concentration dependent retardation coefficient $R(c)$:

$$R(c)\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} \tag{5}$$

with $R(c) = (1 + k^* c^{n-1})$ and $k^* = \frac{\rho}{\theta} nk$. A concentration- or time-dependent retardation coefficient is also obtained for the Langmuir isotherm.

For many substances time dependent sorptive processes were observed and discussed in literature (Gaston and Locke, 1994; Selim et al., 1996). In these cases, linear or nonlinear nonequilibrium models have been used. For nonequilibrium sorption processes different models were proposed in literature:

$$\frac{\partial s}{\partial t} = k_1 c - k_2 s \tag{6}$$

$$\frac{\partial s}{\partial t} = k_1 c^n - k_2 s \tag{7}$$

A more general formulation of Eqs. (6) and (7) is

$$\frac{\partial s}{\partial t} = r(k^q c^{nq} - s^q) \tag{8}$$

where r is a transition rate and q a constant parameter. If the sorption process is in equilibrium, $\frac{\partial s}{\partial t} = 0$ and s and c are lying on a Freundlich isotherm with parameters k and n.

For physical nonequilibrium conditions the mobile/immobile concept was originally introduced by Coats and Smith (1964) and successfully applied by many authors (e.g., van Genuchten and Wierenga, 1977; Parker and van Genuchten, 1984; Vanclooster et al., 1992) to explain accelerated and extensive tailing of solute movement observed in natural soils. In the mobile/immobile model concept the liquid phase is divided in a mobile and an immobile fraction. The exchange between the two phases is described by a rate limited diffusion process. This model is usually applied to explain the nonideal behavior of the BTCs of nonreactive solutes in porous media and is given by:

$$\theta_{\mathrm{m}}\frac{\partial c_{\mathrm{m}}}{\partial t} + \theta_{\mathrm{im}}\frac{\partial c_{\mathrm{im}}}{\partial t} = \mathscr{L}_{\mathrm{m}} c_{\mathrm{m}} \tag{9}$$

$$\theta_{\mathrm{im}}\frac{\partial c_{\mathrm{im}}}{\partial t} = \alpha(c_{\mathrm{m}} - c_{\mathrm{im}}) \tag{10}$$

where θ_{m} is the water content of the mobile phase, c_{m} is the concentration in the mobile phase [M L^{-3}], θ_{im} is the water content of the immobile phase [M^3 M^{-3}], c_{im} is the concentration in the immobile phase [M^3 M^{-3}], and $\mathscr{L}_{\mathrm{m}}$ is the transport operator for the mobile phase defined as $\mathscr{L}_{\mathrm{m}} = \theta_{\mathrm{m}} D_{\mathrm{m}} \frac{\partial^2}{\partial x^2} - U\frac{\partial}{\partial x}$; and D_{m} the dispersion coefficient for the mobile region [L^2 T^{-1}].

In addition to the above processes, hysteretic sorption has been observed in experiments for more than two decades (Miller and Pedit, 1992). Various theories have been postulated to explain this behavior such as: solute degradation or loss during the course of an experiment, slow rates of sorption or desorption kinetics, sorption to nonsettling particles, presence of competing solutes, change in sorbent characteristics as a function of time and formation of site-specific solute–solid bonds. Streck et al. (1995) used a rate-limited two stage kinetic sorption model to explain hysteretic effects. They attributed the occurrence of hysteresis to the fact that equilibrium conditions were not obtained during the experiment. In addition, they found that simazine transport in field lysimeters could not be described by linear or nonlinear equilibrium sorption.

In this paper, we will use a simple hysteretic model to explain measured BTCs of uranin and lithium. In this approach, it is assumed that the sorption–desorption behavior of a substance may be described by two isotherms:

$$s = k_{\mathrm{f}} c^{n_{\mathrm{f}}} \tag{11}$$

for $\frac{\partial c}{\partial t} > 0$, and

$$s = k_{\mathrm{b}} c^{n_{\mathrm{b}}} \tag{12}$$

for $\frac{\partial c}{\partial t} < 0$ where the subscripts f and b refer to adsorption and desorption, respectively. This model will be used to predict experimentally observed BTCs of uranin in column experiments.

2.1. Asymptotic analysis of linear equilibrium and nonequilibrium sorption

Vereecken et al. (1998b) used an asymptotic analysis to examine the long time behavior of solute concentrations in linear equilibrium and nonequilibrium solute transport. Asymptotic analysis is concerned with the evaluation of the concentration evolution for large times at a fixed position in space. It is thereby assumed that time and space variables can be separated for large times ($t \to \infty$) such that asymptotically

$$c(x,t) \sim \gamma(x)\sigma(t) \tag{13}$$

where $\gamma(x)$ and $\sigma(t)$ are functions to be determined. From the analytical solution of convection–dispersion equations with linear sorption processes, we know that the concentration at a fixed position will drop exponentially with time for a pulse type injection. For large times this exponential drop will give a straight line in a log representation of BTCs with a slope equal to $-\beta$. This may be illustrated for the simple problem of the convection dispersion equation with retardation. The model describing this transport process is:

$$R\frac{\partial c}{\partial t} = \mathscr{L}c \tag{14}$$

where R is the retardation coefficient, defined as $R = 1 + \frac{\rho}{\theta}k_{\mathrm{d}}$ and $\mathscr{L}$ is the transport operator defined as $-v\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}$. Substituting Eq. (13) in Eq. (14) and rearranging we obtain

$$\frac{\mathscr{L}\gamma(x)}{R\gamma(x)} = \frac{\partial\sigma(t)}{\partial t}\sigma(t)^{-1} \tag{15}$$

Because the left hand side only depends on x and the right hand side on t, both sides have to be equal up to a constant β according to

$$\beta = \frac{\partial \sigma(t)}{\partial t} \sigma^{-1}(t) \tag{16}$$

with the solution

$$\sigma(t) = \sigma_0 \exp(\beta t). \tag{17}$$

where σ_0 is the initial value of $\sigma(t)$ at time $t=0$. For a pulse type injection concentration follows $e^{-\beta t}$. Expanding $c(x,t)$ in an asymptotic series with coefficients $X_n(x)$ with respect to time for $t \to \infty$, we obtain for c, $\dot{c}$ and $\ddot{c}$

$$c \sim \exp(-\beta t)\left[X_0(x) + t^{-1}X_1(x) + \dots\right] \tag{18}$$

$$\dot{c} \sim \exp(-\beta t)\left[-\beta X_0(x) - (\beta t^{-1} + t^{-2})X_1(x) - (\beta t^{-2} + 2t^{-3})X_2(x)\dots\right] \tag{19}$$

$$\begin{aligned}\ddot{c} \sim \exp(-\beta t)\big[&\beta^2 X_0(x) + (\beta^2 t^{-1} + 2\beta t^{-2} + 2t^{-3})X_1(x)\\ &+ (\beta^2 t^{-2} + 4\beta t^{-3} + 6t^{-4})X_2(x)\dots.\big]\end{aligned} \tag{20}$$

For nonequilibrium transport processes, the expansion of the second order derivative of c with respect to time is needed in order to obtain an equation which only contains c as unknown. By introducing the first term of the expansion for c, $\dot{c}$ and $\ddot{c}$ in the transport equation containing nonequilibrium processes, a linear differential equation of second order with constant coefficients is obtained. For appropriately chosen boundary conditions, an ordinary partial differential equation of the order two or higher in β depending on the type of kinetic sorption considered may then be derived.

Vereecken et al. (1998b) derived relationships between the slope of the BTCs in semi-log representation and transport and sorption parameters for various types of linear nonequilibrium models. Because the two site sorption model (TSEK, equilibrium and linear kinetic sorption) is used in the interpretation of BTCs, the most important steps of the asymptotic analysis and the result are repeated for convenience. For more details, the reader is referred to Vereecken et al. (1998b). The starting point of the derivation is the following equation

$$\frac{\partial c}{\partial t} + \frac{\rho}{\theta}\frac{\partial s}{\partial t}\mathscr{L}c \tag{21}$$

where $\mathscr{L} = -v\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}$

$$s = s_1 + s_2 \tag{22}$$

$$s_1 = k_1 c = Fkc \tag{23}$$

$$\frac{\partial s_2}{\partial t} = \alpha_2(k_2 c - s_2) \tag{24}$$

At equilibrium, the sorption at the s_2 sites is given by

$$s_2 = k_2 c = (1-F)kc \tag{25}$$

where F is the fraction of sorption sites in direct equilibrium, and $1-F$ the fraction of sites undergoing kinetic sorption. k_1 and k_2 represent the distribution coefficients for linear equilibrium sorption.

From the above equations we obtain

$$\frac{\partial c}{\partial t} - \mathscr{L}c + \frac{\rho}{\theta} k_1 \frac{\partial c}{\partial t} + \frac{\rho}{\theta}\alpha_2(k_2 c - s_2) = 0 \tag{26}$$

Taking the derivative of above equation with respect to time, substituting the asymptotic approximations for c, $\dot{c}$, $\ddot{c}$ and rearranging, we find the following linear differential equation of second order

$$D\frac{\mathrm{d}^2 X_0}{\mathrm{d}x^2} - v\frac{\mathrm{d}X_0}{\mathrm{d}x}\frac{1}{\beta - \alpha_2}\left(R\beta^2 - A_1\beta\right)X_0 = 0 \tag{27}$$

where $R_1 = 1 + \frac{\rho}{\theta}k_1$ and $A_1 = \frac{\rho}{\theta}(\alpha_2 k_2 + \alpha_2\,\rho k_1) + \alpha_2$. X_0 is the first coefficient in the asymptotic series of $c(x,t)$ (Eq. (18)). The solution for β using appropriate boundary conditions (Vereecken et al., 1998b) reads:

$$\beta = 0.5\left(\frac{A_1}{R_1} + \frac{v^2}{4DR_1} - \sqrt{\left(\frac{A_1}{R_1} + \frac{v^2}{4DR_1}\right)^2 - \frac{4\alpha_2 v^2}{4DR_1}}\right) \tag{28}$$

For the case of simple linear retardation the asymptotic behavior becomes:

$$\beta = \frac{v^2}{4DR} \tag{29}$$

The asymptotic behavior for the mobile/immobile model reads (Vereecken et al., 1998b)

$$\beta = 0.5\left(\alpha^* + \frac{U^2}{4D_\mathrm{m}\theta_\mathrm{m}} - \sqrt{\left(\alpha^* + \frac{U^2}{4D_\mathrm{m}\theta_\mathrm{m}}\right)^2 - \frac{\alpha U^2}{D_\mathrm{m}\theta_\mathrm{m}\theta_\mathrm{im}}}\right) \tag{30}$$

where $\alpha^* = \alpha\frac{\theta}{\theta_\mathrm{im}}$ with $\theta = \theta_\mathrm{im} + \theta_\mathrm{m}$.

2.2. Asymptotic analysis of nonlinear equilibrium sorption

Jaekel et al. (1996) used asymptotic analysis for the case of solutes undergoing nonlinear equilibrium sorption defined by a Freundlich isotherm (Eq. (4)). As for the linear nonequilibrium cases they exploited the fact that

$$c(x,t) \sim \gamma(x)\sigma(t) \tag{31}$$

with γ, σ functions to be determined. Due to advection and the finite spatial and temporal extension of the source, the concentration at any fixed position x is approaching 0 for $t \to \infty$. Therefore, they neglect the 1 compared to $k^* c^{n-1}$ in Eq. (5) for sufficiently large t. With these assumptions they obtain

$$\frac{\mathscr{L}\gamma(x)}{k^*\gamma(x)^n} = \sigma(t)^{n-2}\frac{\partial\sigma(t)}{\partial t} \tag{32}$$

where the left hand side depends only on x and the right hand side only on t. Thus both have to be equal to a constant, say λ, such that

$$\frac{\partial\sigma(t)}{\partial t} = \lambda\sigma(t)^{2-n} \tag{33}$$

with the general solution

$$\sigma(t) = (\lambda(n-1)t + \text{const})^{1/(n-1)} \tag{34}$$

One then obtains

$$c(x,t) \sim t^{-\alpha}\gamma(x) \quad \text{for } t \to \infty \tag{35}$$

with $\alpha = 1/(1-n)$, where all multiplicative constants were shifted to γ. For this choice $\sigma(t) = t^{-\alpha}$ with the constant $\lambda = \theta^{n-2}\dot{\sigma}$ equal to $-\alpha$ such that γ fulfills the differential equation

$$-k^{*}\alpha\gamma(x)^{n} = \mathscr{L}\gamma(x). \tag{36}$$

Hence Jaekel et al. (1996) showed that separability leads to the asymptotic behavior

$$c(x,t) \propto t^{-1/(1-n)} \quad \text{for } x \text{ fixed and } t \to \infty. \tag{37}$$

From Eq. (37) breakthrough curves should decrease asymptotically in time like a power law with an exponent $-1/(1-n)$. In this analysis no assumptions about the form of the transport operator $\mathscr{L}$, apart from linearity, need to be made.

2.3. Asymptotic analysis of nonlinear nonequilibrium sorption

A similar asymptotic analysis was done by Wendt and Jaekel (1998) for the case of nonlinear nonequilibrium described by Eqs. (1) and (8). Assuming that both s and c decay asymptotically with power laws in time at a fixed position we can write:

$$c(x,t) \sim \gamma(x)t^{-\alpha} \tag{38}$$

$$s(x,t) \sim \sigma(x)t^{-\beta} \tag{39}$$

for $t \to \infty$. From Eq. (1) one arrives at

$$-\beta\sigma t^{-\beta-1} \sim t^{-\alpha}\mathscr{L}\gamma \tag{40}$$

such that $\alpha = \beta + 1$. Using this result in Eq. (8) they showed that there are two different cases (if $n < 1$): $qn \leq 1$ and $qn > 1$. In the first case, the two terms of the RHS of Eq. (8) balance and the equilibrium result

$$\alpha = 1/(1-n) \tag{41}$$

is obtained. In the second case, $s^q \gg k^q c^{nq}$ for large times ($t \to \infty$), such that $\frac{\partial s}{\partial t} \approx -rs^q$. This leads to a modified exponent different from the equilibrium case:

$$\alpha = 1/(q-1) \tag{42}$$

3. Materials and methods

Sediment samples were collected from two different sites within an unconfined aquifer consisting of quaternary fluviatile sediments. Samples V1–V9 were taken from the aquifer at the Krauthausen field site (Vereecken et al., 1998a). Sediment V10 was taken from the same aquifer but about 6 km north of the experimental field site. The sediment samples were air dried and passed through a 2 mm sieve prior to use. On these sieved fractions basic sediment properties were determined (Table 1). Aqueous solutions of uranin, LiCl and NaBr were used as input solutions for both batch and column displacement studies using tap water stemming from the same aquifer. The background concentrations of Li^+ (hereafter lithium), Cl^- (hereafter chloride) and Br^- (hereafter bromide) were 0.002 mg l^{-1}, 53 mg l^{-1}, 0.07 mg l^{-1}. The observed BTCs were corrected for these background concentrations. Uranin is the trade mark for di-natrium fluorescein ($C_{20}H_{10}O_5Na_2$) which is frequently used as a dye tracer in hydrogeology. In the batch and column displacement studies, uranin and LiCl were applied as a mixture (except for V8 and V9 in which NaBr was used rather than LiCl) in order to mimic the condition which occurred during a natural tracer experiment conducted at the Krauthausen field site (Vereecken et al., 1998a,b). Extensive work of Döring (1997) showed that in these concentration ranges there is no interaction between uranin and lithium for the sorption sites. Uranin was determined with fluorescence spectroscopy (measurement error: 3–5%) up to a detection limit of about 0.01 μg l^{-1}. Lithium was determined with IPC-MS with a measurement error of at maximum 7% and a detection limit of about 10 μg l^{-1}. Chloride and bromide were determined using ion chromatography with an error of 3–5%. The detection limits for these anions were below background concentrations.

3.1. Column displacements experiments

Two sets of column displacement studies were performed. In the first set, breakthrough curves of uranin, lithium, chloride and bromide were measured on sediment samples V1 to V9. Nine steel columns (diameter 50 mm, height 300 mm) were packed with dried and sieved material following the procedure given by Klotz (1979). The columns were run under saturated conditions with a steady-state flow directed from the

Table 1
Physico-chemical properties of the nine sediment samples

Column	2–0.05 [mm]	0.05–0.002 [mm]	< 0.002 [mm]	Corg [%]	CEC [$mmol_{equ}$]	u	K [m/s]	SSA [m^2/g]	Depth [m]
V1	96.0	1.8	2.2	0.2	0.5	8.2	1.8e−4	0.5	6.6–6.8
V2	97.6	0.8	1.6	0.6	0.4	3.9	6.4e−4	0.5	1.0–2.1
V3	94.2	3.2	2.6	0.1	1.1	6.6	1.8e−4	0.7	5.4–6.3
V4	93.4	3.7	2.9	0.2	1.4	8.1	6.6e−5	0.9	7.8–8.7
V5	94.6	2.3	3.1	0.1	1.3	7.3	4.7e−5	1.1	8.5–9.8
V6	92.6	4.1	3.3	0.2	1.5	9.8	3.3e−5	1.0	3.3–3.7
V7	87.3	4.9	4.8	0.2	1.3	12.9	1.e−5	1.3	3.3–3.7
V8	89.9	5.6	4.5	0.3	1.6	11.8	1.2e−5	1.2	2.6–3.2
V9	95.6	1.1	2.9	0.3	0.8	9.1	2.2e−5	0.8	3.7–4.3
V10									9.0–10.0

K is the hydraulic conductivity of the sediment, u is the uniformity coefficient of the grain size distribution and SSA is the specific surface area.

bottom to the top using a peristaltic pump. The tracer mixtures were added in a short pulse. The leachate was sampled over 10-min intervals using an automated fraction collector. Experimental details for the different soil columns are shown in Table 2.

In the second set, three steel columns (100 mm diameter, 400 mm height) were packed with sediment V10 following the same procedure as for set 1. The columns were run in the same manner as for set 1. Three different mean pore velocities were imposed: column V10R1 with a velocity v equal to 0.0076 cm min^{-1}, V10S1 with $v = 0.057$ cm min^{-1} and V10G1 with $v = 0.13$ cm min^{-1}. Uranin and LiCl were applied as a mixture with concentrations given in Table 2. The sampling equipment for the leachate was identical as for set 1. The purpose of using different velocities was to analyze the change in the tailing of the BTCs of uranin, lithium and chloride.

3.2. Batch studies

Two sets of batch studies were conducted. In the first set the sorptive behavior of lithium and uranin was determined on the sediments V1–V8 for uranin and on sediments V1–V7 for lithium. Data points on the isotherms were determined for three different initial concentrations (uranin: 5, 50 and 500 μg l^{-1}; lithium: 90, 900, 9000 μg l^{-1}). Döring (1997) showed that three data points provided a good estimate of the Freundlich parameters. Points of the isotherm were determined by equilibrating 50 mg of sediment with an aqueous solution of 30 ml. On the basis of kinetic experiments (Döring, 1997) an equilibration time of 48 h was selected for each data point on the isotherm. After equilibration, the samples were allowed to sediment for 3 h. Then an aliquot of 10 ml from the supernatant was taken, filtrated and analyzed for uranin and lithium.

In the second set, adsorption–desorption batch experiments were conducted on sediment V10. Fifty milligrams of sediment were equilibrated again with 35 ml of an aqueous solution containing uranin. The equilibrium adsorption isotherm was deter-

Table 2
Parameters for the column experiments

Column	v [cm min^{-1}]	Porosity	Pulse time [min]	c_0 Uranin [mg l^{-1}]	c_0 Li$^+$ [mg l^{-1}]	c_0 Cl$^-$ [mg l^{-1}]	c_0 Br$^-$ [mg l^{-1}]
V1	0.17	0.30	10.0	67.7	486	2430	–
V2	0.17	0.29	10.0	54.1	451	–	–
V3	0.17	0.30	10.0	54.1	451	230	–
V4	0.12	0.25	16.7	61.6	5200	36400	–
V5	1.7	0.30	1.0	44.7	426	2280	–
V6	0.12	0.25	16.7	69.5	5900	36500	–
V7	0.17	0.28	1.0	67.6	486	2250	–
V8	0.12	0.25	16.7	54.0	–	–	1820
V9	1.7	0.3	1.0	–	–	–	2370
V10R1	0.0076	0.33	16.0	66.0	438	2252	–
V10S1	0.06	0.33	2.5	55.0	73	377	–
V10G1	0.13	0.3	1.0	55.0	73	377	–

mined starting from six initial concentration levels: 0.57, 0.29, 0.15, 0.057, 0.029 and 0.0057 mg l^{-1}. The samples were shaken for 1 min with a stop of 30 min during a period of 48 h. After this period, the samples were allowed to settle for a period of 3 h. Then an aliquot (10 ml) of the supernatant was taken, filtrated and analyzed using fluorescence spectroscopy. For the four highest concentrations, the removed volume was replaced by solution free water and equilibrated for 48 h using the same procedure as above. The procedure of removing and replacing the supernatant was repeated 11 times in order to obtain the desorption branch of the adsorption isotherm. The equilibration time for desorption was determined on the bases of desorption studies conducted on 25 replicate samples. The 25 samples were equilibrated with a solution of 0.100 mg l^{-1} of uranin for 48 h. After sedimentation, 10 ml of the supernatant was removed and replaced with a solution free water. Equilibration was then controlled for 48, 96, 192 and 384 h, respectively. This procedure was repeated 11 times in order to determine the desorption isotherm. Comparison of the different times showed that no statistically significant change in the concentration was found after 48 h.

3.3. Parameter estimation

In addition to the asymptotic analysis, BTCs were analyzed using the CXTFIT program of Parker and van Genuchten (1984). For those BTCs showing hysteretic behavior the program FRETRA was written. This program solves Eq. (1) combined with Eqs. (11) and (12) using implicit finite differences. The nonlinearity of the resulting matrix equation is solved using the Newton–Raphson method (Press et al., 1992). The top boundary condition was defined as:

$$vc_0 = vc(z=0,t) - D\frac{\partial c}{\partial z} \tag{43}$$

The bottom boundary condition was described following:

$$\frac{\partial c(z=L,t)}{\partial z} = 0 \tag{44}$$

Hysteresis was defined by Eqs. (11) and (12) using n_f, n_b and k_f as input parameters. k_b was calculating in the program from $k_\mathrm{b} = \frac{s}{c^{n_\mathrm{b}}}$.

4. Results and discussion

4.1. Analysis of experiments with bromide and chloride

In a first step, the observed bromide and chloride BTCs of set 1 were analyzed qualitatively using results from asymptotic analysis. For an inert tracer injected as a Dirac delta pulse we expect the concentration to drop with $e^{-\beta t}$ for large times. This should give a straight line behavior of the tailing in a log representation. For the BTCs corresponding to the sediments V1, V3, V5, V6, and V7 an almost straight line behavior may be observed (Fig. 1). Therefore, the CDE with a linear retardation coefficient is a first good model choice to describe the data. Results of the estimated parameters are

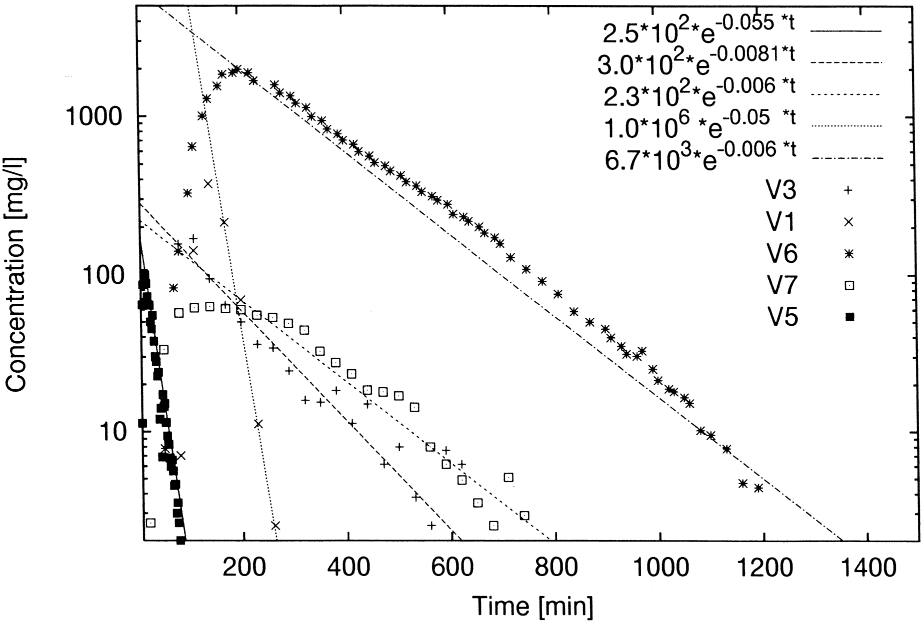

Fig. 1. Log representation of chloride breakthrough curves of set 1. The straight lines represent the long time behavior obtained from asymptotic analysis.

shown in Table 4. In addition to the fitted parameters the column Peclet number is calculated as $P_e = Lv/D$. In Fig. 2, the model fit is compared to the measured BTCs. The parameter were estimated with the CXTFIT code (Parker and van Genuchten, 1984). Adjusting Eq. (1) with linear retardation gives a good agreement between measured and calculated concentrations as is indicated by the high r^2 values for V1, V5, V6 and V7 (Table 4). A comparison between the estimated dispersion coefficient D using CXTFIT and the calculated dispersion coefficient $D_a = v^2/4\beta$ from the asymptotic analysis is only warranted when the solute is really conservative. For sediment V5, with R almost equal to 1, a good agreement between both dispersion coefficients is found. Also the other sediments with retardation coefficients slightly different from 1 show similar values for D and D_a. Thus for a conservative tracer, a first good guess of D can be obtained from the evaluation of the slope of the tailing part of a BTC in logarithmic representation.

Although a straight line behavior was observed for the BTC of sediment V3, the tailing is not well described by the CDE with retardation coefficient. The use of the mobile/immobile model, as suggested by the value of $R < 1$, did not provide a better description of the data. Also a log–log plot of this BTC did not suggest the need for a transport operator which is nonlinear. The noisy behavior of the measured concentrations was not observed in the BTCs of lithium and uranin suggesting that errors in the determination of the concentration might have occurred.

For the bromide BTC of sediment V9, a linear behavior in a log–log representation was found suggesting the presence of nonlinear sorption or the presence of intra-aggre-

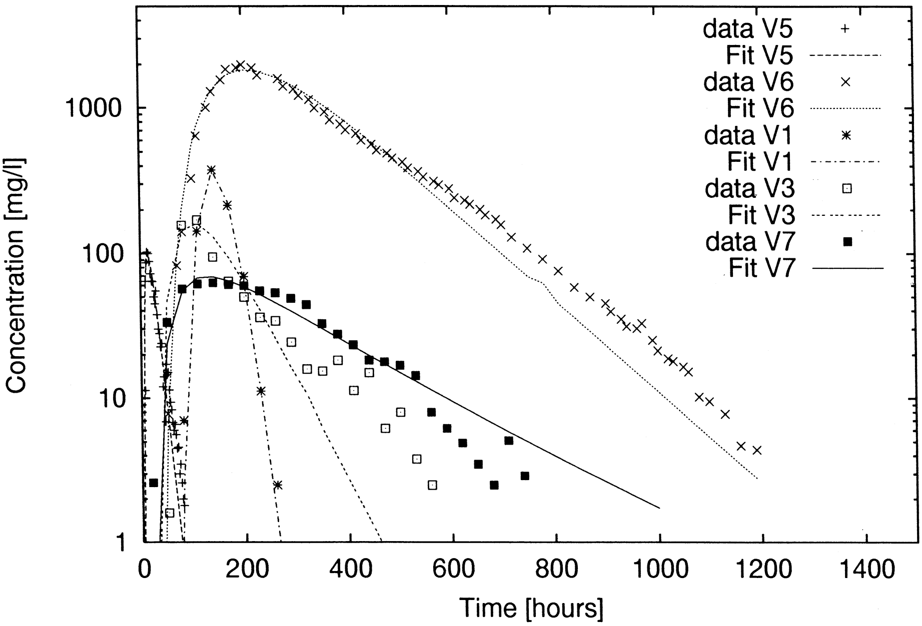

Fig. 2. Fitted CDE with retardation to the observed chloride BTCs of set 1 showing a linear asymptotic behavior.

gate diffusion (not shown). Fitting a CDE with linear equilibrium sorption or using the mobile/immobile concept did not provide an acceptable description of the measured concentrations in the tailing of the BTC. For intra-aggregate diffusion, described as a Fickian diffusion process, the asymptotic behavior of the concentration drops with $t^{-3/2}$ (Gratwohl, 1998). The slope of the tailing part of the BTC, however, was found to be equal to -3. This indicated that intra-aggregate diffusion is not the mechanism dominating the long-time behavior. Nonlinear sorption described by Freundlich equation also results in a straight line behavior in log–log representation. In this case the sorption of bromide would occur with a Freundlich exponent n equal to 0.66. No batch sorption were conducted with bromide to verify this hypothesis. However, the BTC of chloride for sediment V5, having an identical mean pore water velocity, mean porosity and similar sediment properties (Table 1) was well described with the CDE. A possible explanation for the observed behaviour of bromide in sediment V9 may be the presence of oxides on which bromide may be sorbed.

The BTC of V4 (Fig. 3) shows a combination of two straight lines with different slopes. This is a typical behavior for a two site/two region model (Vereecken et al., 1998b). In case the solute is undergoing chemical sorption, the first slope mainly reflects that part of the bulk mass which undergoes equilibrium linear sorption or fast linear kinetic sorption. The second part of the tailing represents the part of the mass undergoing e.g., slow linear kinetic sorption. The deviation from the straight line for the very low concentrations might result from a small experimental error in the determination of the background concentration which was subtracted from the measured concen-

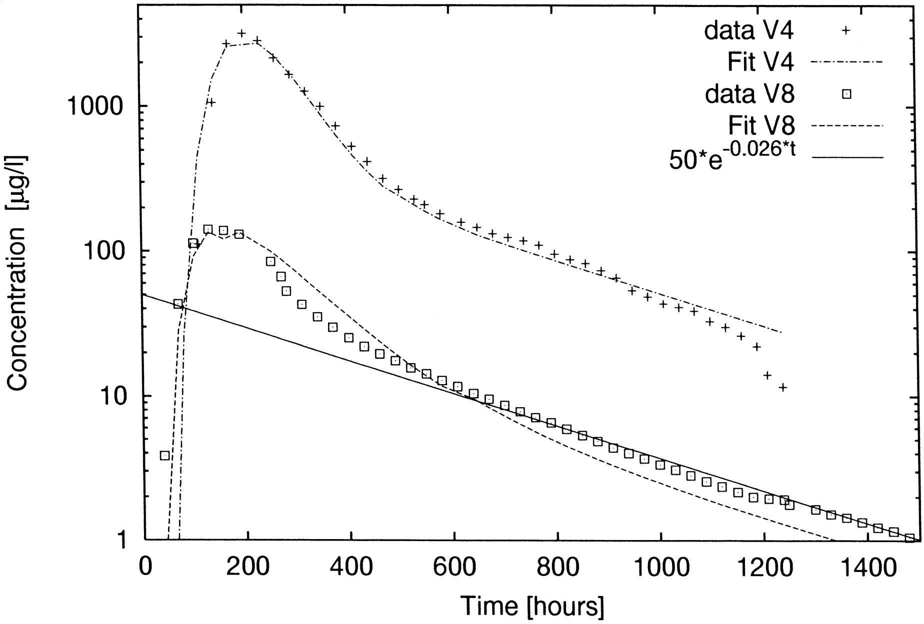

Fig. 3. Log representation of chloride (V4) and bromide (V8) breakthrough curves for set 1. The straight line represents the long time behavior obtained from asymptotic analysis. The dashed lines show the fit of the mobile/immobile model to the data.

tration values. Fitting Eq. (9) to the observed BTC shows a very good agreement (Fig. 3). The parameters were fitted by trial and error because the ordinary least squares estimator used in the model does not account for the smaller concentration in the tail. The correlation coefficient r^2 was equal to 0.97 with $R = 1.38$, $\theta_m / \theta = 0.73$ and $\alpha = 0.0029$ min^{-1}. The velocity was equal to 0.12 cm min^{-1}, $D = 0.22$ cm^2 min^{-1}, with a pulse of 1820 mg l^{-1} for about 16 min. This results in a Peclet number which is equal to 16.4. The value of the Peclet number will be important for the interpretation of the tracer experiments with uranin and lithium. Also V8 is well described by a mobile/immobile model. The following parameters were estimated: $R = 1.23$, $\theta_m / \theta = 0.82$, $\alpha = 0.0025$ min^{-1}. The mean pore water velocity was equal to 0.12 cm min^{-1}, $D = 0.50$ cm^2 min^{-1}. The injection concentration and pulse time were taken from Table 2. These values are similar to the ones obtained for V4. Both α values are in perfect agreement with the slope estimated from asymptotic behavior. This suggests that this slope may be used to provide information on the value of α. In addition the asymptotic value can be used to corroborate estimates obtained from inverse methods.

The chloride BTCs of set 2 were excellently described by the CDE equation. Only the value of the dispersion coefficient was fitted using CXTFIT. The use of the asymptotic analysis resulted in values of β for the CDE (Eq. (29)) equal to 0.76($\pm$0.3), 5.9($\pm$0.21) and 14.6($\pm$1). The calculated dispersion coefficient from asymptotic analysis for V10R1, V10S1, V10G1 were larger than those obtained from CXTFIT. This may be due to the fact that the asymptotic behavior was not observed because of the rather high background concentration for chloride which makes it impossible to measure the tailing over more than two orders of magnitude.

4.2. Analysis of experiments with uranin

Batch experiments conducted by Döring (1997) on sediment from the Krauthausen field site showed that uranin sorbs in a nonlinear manner which could be described by a Freundlich isotherm. In this study, batch experiments were conducted on 8 sediment samples following the method described above. Results of our batch experiments (Table 3) show that uranin sorbs in a nonlinear manner with the Freundlich n parameter varying between 0.78 and 1.04. The k_f values vary between 0.07 and 0.46. Regression analysis showed that the k_f parameter is positively correlated with organic carbon content ($r = 0.84$), with cation exchange capacity ($r = 0.77$), with the percent of clay content ($r = 0.76$) and with the specific surface area ($r = 0.89$).

From asymptotic analysis we know that for a pulse injection of substances which sorb according to a Freundlich isotherm, the breakthrough curve at a certain distance from the injection will drop with $t^{-\alpha}$ for large times. In this case $\alpha = 1/(1-n)$ with n equal to the Freundlich exponent. Thus in a log–log representation, the tail of a BTC should drop as a straight line. A clear straight line behavior is found for the sediments V3, V5 and V8 in Fig. 4. Fitting a straight line through the tailing part of these BTCs gives a value for $\alpha = 3.2$ and thus a value of $n = 0.69$. As a reference, the expected large time behavior of the concentration based on the exponent obtained from the batch experiments (mean value equal to $n \sim 0.85$ or $t^{-6.6}$) is given in Fig. 4. The calculated P_e values for these three experiments range between 1.2 and 7.2 (Table 4).

The difference in the n exponent values between batch and column experiments may be explained by the simple hysteresis model presented above. FRETRA was used to calculate the observed BTCs of uranin for sediment V3, V5 and V8. The transport parameters were taken from the experiments with bromide, the n_f value was taken from the batch experiments, and the value of n_b was estimated from asymptotic theory. The k_f values were also taken from batch experiments. Initial pulse concentration and pulse duration are determined by the experimental setup. Excellent agreement is obtained for

Table 3
Fitted parameters of the Freundlich isotherm for the uranin batch experiments

Sediment	k_f [μg kg^{-1} (l μg^{-1})^n]	n
V1	0.07	1.04
V2	0.15	0.89
V3	0.11	0.97
V4	0.24	0.86
V5	0.27	0.83
V6	0.41	0.78
V7	0.41	0.78
V8	0.46	0.82

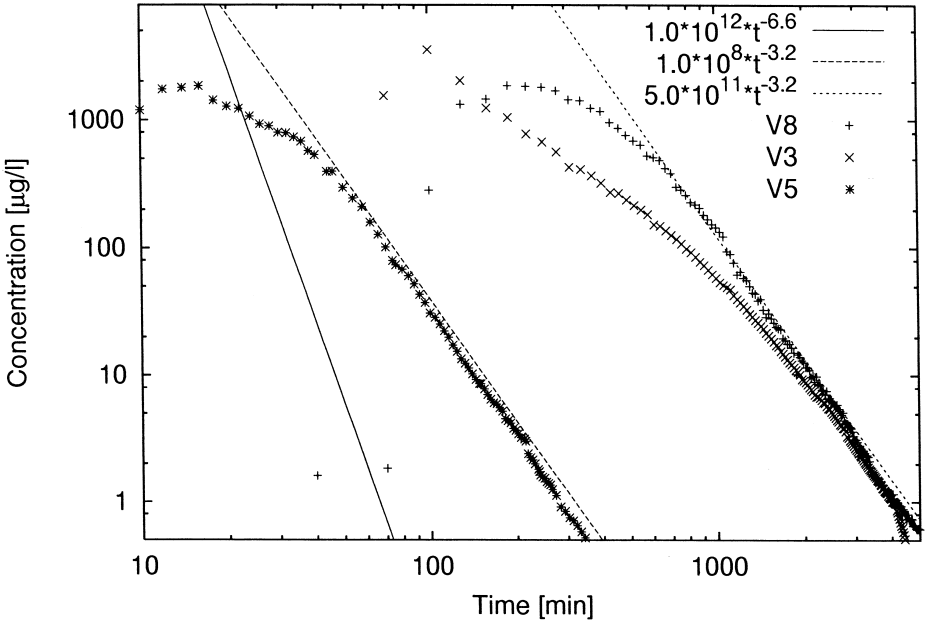

Fig. 4. Double log representation of the uranin BTCs for sediments V3, V5 and V8.

the uranin BTCs with sediment V5 and V8 (Fig. 5). For sediment V5 only a slight increase of the batch k_f parameter to a value of 0.4 was needed to obtain this result. We consider this a remarkable result because all measured parameters were directly used to calculate the observed behavior. For sediment V8 the mean velocity was increased with 20% in order for the calculated BTC to match the measured one. This increase is justified by the presence of 20% of immobile water for sediment V5 as obtained from the BTC of chloride. The presence of this immobile water leads to a higher mean pore

Table 4
Fitted parameters with CDE for chloride and bromide, v is the mean pore velocity, c_0 is the injection concentration, T is the pulse duration, D is the dispersion coefficient, R is retardation, P_e is the column Peclet number, D_a is the dispersion coefficient estimated from asymptotic theory and r^2 is the coefficient of determination

Column	v [cm/min]	c_0 [mg/dm^3]	T [min]	D [cm^2/min]	R	D_a [cm^2/min]	P_e	r^2
V1	0.17	2481.2	10.0	0.09	0.8	0.14	56.6	0.99
V3	0.17	2238.1	10.0	0.69	0.7	0.90	7.2	0.93
V5	1.7	2287.0	0.95	9.1	1.1	13.2	5.6	0.96
V6	0.16	36520	14.8	0.69	1.4	1.1	6.8	0.99
V7	0.18	2253.0	10.0	6.9	1.3	1.53	2.7	0.96
V10R1	0.0076	2252	16	0.005	1.0	0.01	107	0.99
V10S1	0.057	377	2.5	0.03	0.9	0.08	202.5	0.99
V10G1	0.13	377	1.0	0.06	1.0	0.1	256	0.99

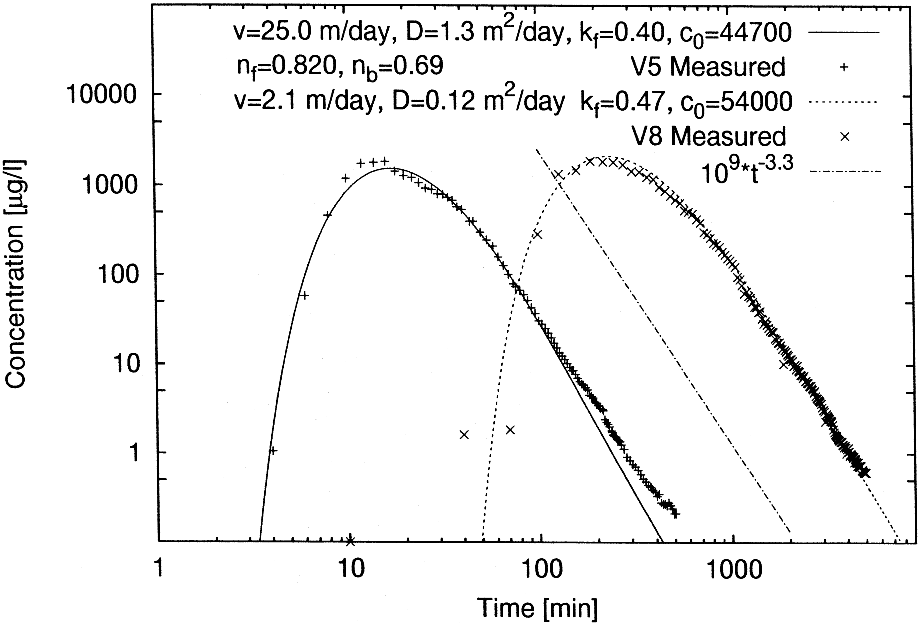

Fig. 5. Calculated and measured BTCs of uranin using a hysteretic model for sediment V5 and V8.

water velocity. Although there is some variation in the sediment properties of the samples V5 and V8, the *n* values are identical. This indicates that the selected sediment parameters do not seem to correlate with the *n* parameter and that other sediment properties influence nonlinear sorption behavior of uranin.

The BTC of sediment V3 in log–log representation gives an almost straight line between 1 and 100 $\mu g\ l^{-1}$ which suggest a Freundlich type sorption. However, a deviation is present from this line at concentrations lower than 1 $\mu g\ l^{-1}$ which cannot be described by the transport model with hysteresis. The deviation cannot be attributed to the presence of a very slow kinetic process because then the deviations should be above the straight line and not below. Most likely changes in experimental conditions occurred which were beyond control. Neglecting these very low concentrations, a good description with hysteretic Freundlich sorption was obtained.

A different behavior of uranin is found for the samples V1 and V4. In Fig. 6, a log–log representation of the sediment samples V1 and V4 is given. For V1 a straight line behavior may be observed over a concentration range between 10 and 0.5 $\mu g\ l^{-1}$. However, the slope is different from the ones observed in Fig. 4. Under the assumption of Freundlich sorption it gives a value of $n = 0.5$ whereas the sediments V5, V8 and V3 gave *n* values equal to 0.69. If uranin would exhibit the same hysteretic behavior used to explain the BTCs for V3, V5, and V8, a similar value of *n* should have been found. In addition, the observed tailing behavior of V3 could not be described by hysteretic Freundlich using n_b values equal to 0.69 and 0.50. For large times, FRETRA underestimated the tail by at least a factor 100 in the concentration. The difference in slopes

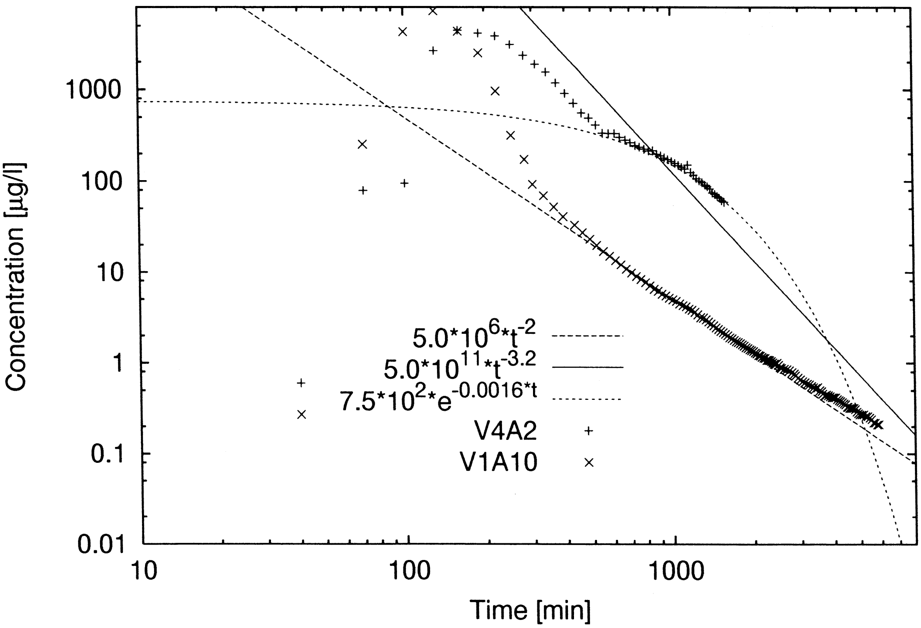

Fig. 6. Log–log representation of the BTCs for sediment V1 and V4. Straight lines show the expected asymptotic behavior.

between V4 and V3, V5, and V8 may, however, be explained by the presence of nonlinear nonequilibrium conditions as described by Eq. (8). Asymptotic analysis of Eq. (8) results in two different cases for $n < 1$: $nq \leq 1$ and $nq > 1$. In the first case the asymptotic behavior has to be the same as in the equilibrium case. This is however not supported by the observed values of the slope which results in n-values which are smaller than those for Freundlich equilibrium sorption. The second case gives an asymptotic behavior of $\alpha = \frac{1}{(q-1)}$. For an α value equal to 2, q is equal to 1.5. Qualitative evaluation of numerically calculated BTCs using Eq. (1) with Eq. (3) with various values of n showed a good agreement with the observed BTCs for sediment V1.

V4 shows a straight line behavior in logarithmic representation with two different slopes. Such a behavior can be perfectly well described with the two site sorption model TSEK. Because transport of chloride in sediment V4 was best described by the mobile/immobile concept D_m and v_m were taken from this experiment. v_m was equal to $v/0.73 = 0.16$ cm min^{-1} and D_m to $D/0.73 = 0.28$ cm^2 min^{-1}. The estimated parameters are $R = 2.1$, $F = 0.05$ and $\alpha = 0.0018$ min^{-1}. The fact that both BTCs show a nonequilibrium behavior for uranin transport whereas the BTCs of sediments V5 and V8 show equilibrium hysteresis may be due to differences in values of P_e. The BTCs of sediments V3, V5 and V8 have P_e values ranging between 1.2 and 7.2. P_e values for the transport in sediments V1 and V4 obtained from the chloride BTCs were equal to 56.6 and 18, respectively. For relative small P_e values the dispersive mixing is occurring at the same time scale as the advective transport such that equilibrium conditions are prevailing. For large P_e values the sorption/desorption becomes time dependent because solute molecules do not have time to equilibrate with the sorption sites. This may result in either linear or nonlinear kinetic sorption.

The three remaining sediment samples V2, V6 and V7 did not show a clear behavior both in logarithmic and log–log representation. None of the proposed models could therefore be used to qualitatively describe the observed behavior. Either asymptotic behavior was not yet reached or a combination of different sorption mechanisms are acting on the solute. This can be e.g., a two site sorption model with sites interacting according to a fast but linear kinetic process and sites with a slow but nonlinear nonequilibrium process. Eventually more than two sites (multi-site model) with different kinetic processes may be responsible for the observed behaviour.

Results of the sorption/desorption experiments for sediment V10 with uranin are given in Fig. 7. The adsorption isotherm showed a clear nonlinear behavior which could be best fitted by a Freundlich equation described as $\log_{10}(s) = -0.41 + 0.85c$. The standard deviation on the intercept $(\log_{10}(k))$ and slope (n) were equal to 0.03 and 0.04, respectively. The four desorption branches could also be described by a Freundlich type equation, however, with different n and k values. The slope of the desorption branches ranges between 0.55 and 0.40. The equations shown in Fig. 7 were obtained by fitting a Freundlich type equation through the data point left of the adsorption isotherm. The standard estimate for the three n values ranged between 0.01 and 0.02. As will be shown later in the asymptotic analysis of the observed uranin BTCs, an excellent

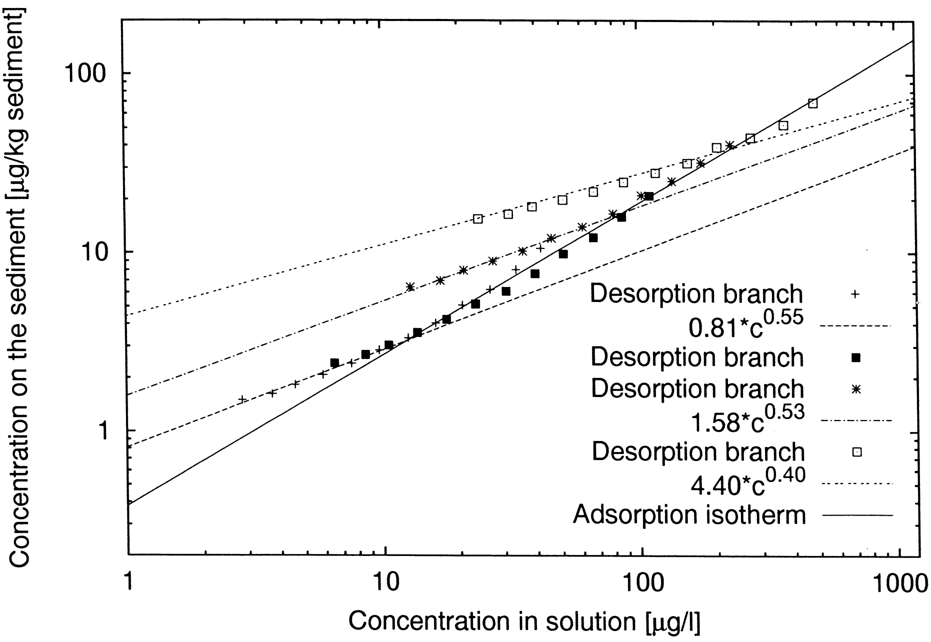

Fig. 7. Sorption/desorption isotherm of uranin for sediment V10.

agreement is found between the estimates of n from the desorption isotherm and the estimates of n obtained from the tailing of the BTCs. The sorption/desorption study clearly shows that the sorption–desorption process of uranin has a hysteretic behavior.

A log–log representation of the uranin BTCs of set 2 shows two important elements. Firstly, the slope of the tails tends to become linear suggesting that the transport process involves a Freundlich type sorption. Secondly, the values of the slopes for V10R1, V10S1 and V10G1 are equal to 2.3, 2.0 and 1.8, respectively. Using the asymptotic analysis for CDE with Freundlich sorption, the n coefficient becomes equal to 0.56, 0.5 and 0.45. These values are in good agreement with the n values obtained from the desorption experiments done on the same sediment.

Fig. 8 shows also the calculated BTCs obtained by using the FRETRA program. The BTCs were predicted in two steps. In a first step, the BTC of column V10R1 was calculated using parameters from independent measurements. The velocity and initial pulse were taken from Table 2, and the dispersion coefficient was obtained from the chloride experiment. The values of k_f, n_f were taken from the adsorption/desorption experiment. The value of n_b was taken from the asymptotic analysis. Using these values, a too strong retardation was obtained for the calculated BTC due to the too high value of k_f. By trial and error we changed the value of k_f to 0.05. As can be seen, this resulted in a good agreement between measured and calculated BTC. Only the tailing is underestimated but the qualitative behavior is well described. In a more classical representation (without log transformation) the calculated BTC would coincide perfectly well with the measured one.

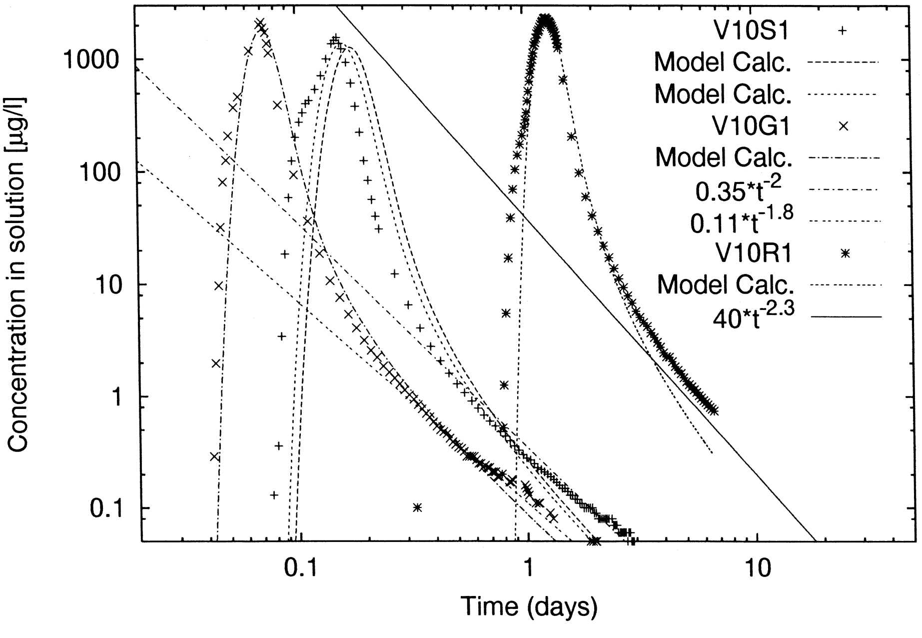

Fig. 8. Calculated and measured uranin BTCs of set 2.

In a second step, the BTCs of V10S1 and V10G1 were calculated. No fitting of the parameters was done in this step. The velocities and initial pulses were taken form Table 2. The dispersion coefficient was taken from Table 4. The value of n_f and n_b were taken from the batch experiment and asymptotic analysis. The value of k_f was fixed to 0.05 (Fig. 8). A perfect agreement is found for V10G1 and this over the whole concentration range. Only for sediment V10S1 a too strong retardation of the BTC was calculated. This may be due to either a too low velocity or too high k_f value. Decreasing the value of k_f resulted in a stronger underestimation of the tailing behavior. We also calculated the BTC using a velocity of 0.19 cm min^{-1}. This value was obtained from the chloride BTC by fitting v and D; but in keeping R equal to 1, a clear difference remained still.

4.3. Analysis of lithium

Results from the batch experiments with lithium are given in Table 5. The isotherms were well described by a Freundlich equation with a n exponent ranging between 0.50 and 0.61. From these batch experiments, a straight line behavior of the tailing of lithium BTCs in log–log representation may be expected. This is actually the case for the tailing of the lithium BTCs of sediments V2, V3, V5 and V7 (Figs. 9 and 10). As a reference, the expected slope of the BTCs from asymptotic theory with the n exponent of 0.5 derived from batch is given by the full line (1×10^3 t^{-2}). For V1, V4 and V6 a straight line in logarithmic representation is found and thus a linear sorptive behavior, either under equilibrium or nonequilibrium conditions, may be assumed (Fig. 12). Note that V1 and V4 were also the cases were kinetic sorption behavior was observed for uranin. This finding contradicts the batch experiments in which lithium sorption was best described by a Freundlich isotherm.

The two site sorption model TSEK was fitted to the BTCs of sediments V1, V4 and V6 using CXTFIT. An additional improvement of the parameter values by trial and error was however needed to improve the fit to the tailing part of the BTCs. Only R, F and α were estimated by fitting. Results are shown in Figs. 11 and 12. For V1, R was found to be equal to 1.4, $F = 0.47$ and $\alpha = 0.00093$ min^{-1}. D was taken from the bromide BTC, the mean velocity v, the concentration of the injection volume and pulse duration were taken from Table 2. For V4, R was estimated to be equal to 2.53, $F = 0.47$ and

Table 5
Fitted parameters of the Freundlich isotherm for the lithium batch experiments

Sediment	k_f [μg kg^{-1} (l $\mu\text{g}^{-1})^n$]	n
V1	0.37	0.46
V2	0.47	0.5
V3	0.53	0.5
V4	0.59	0.5
V5	0.69	0.61
V6	0.92	0.61
V7	0.92	0.54

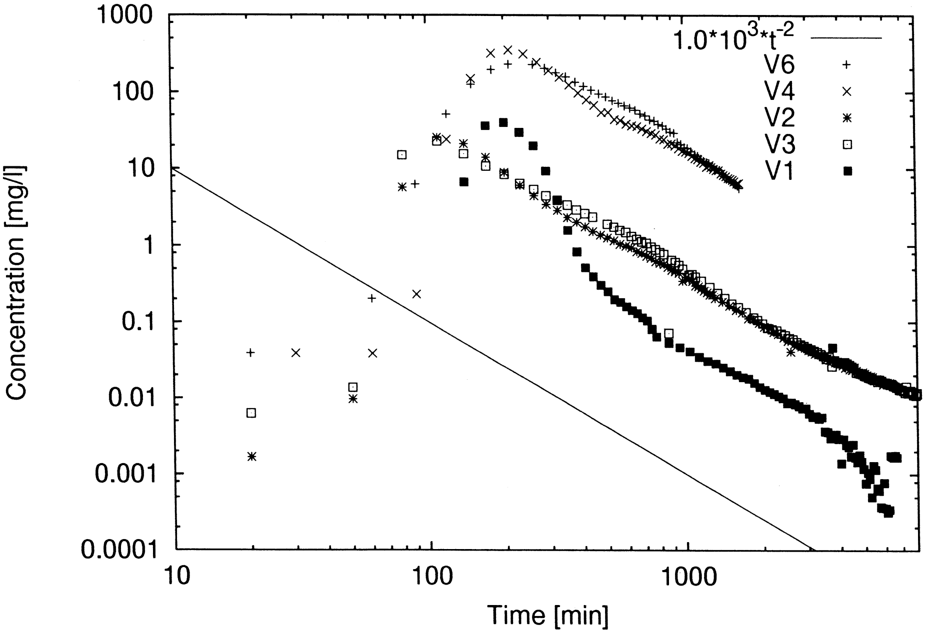

Fig. 9. Log–log representation of the measured lithium breakthrough curves of set 1.

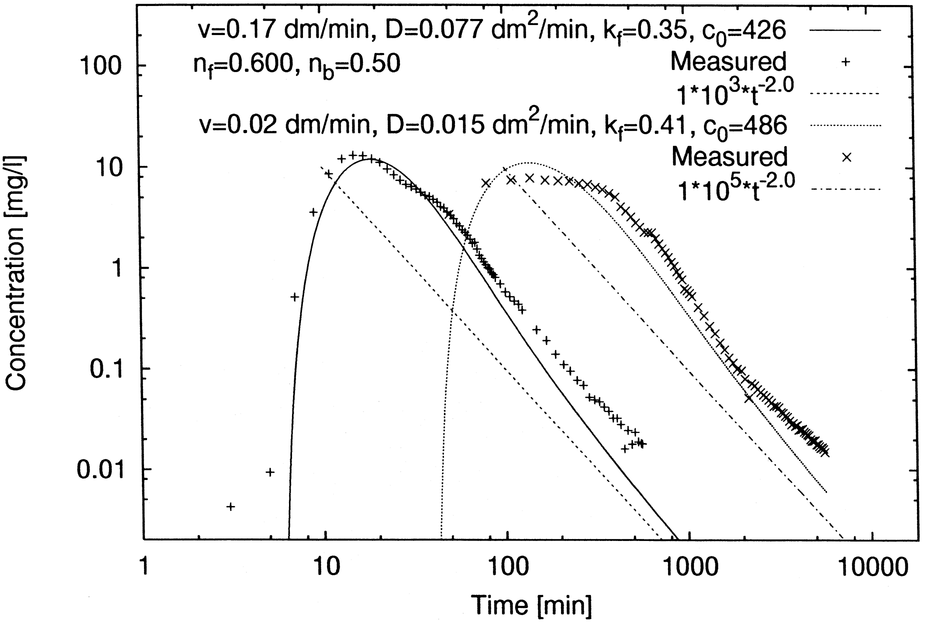

Fig. 10. Calculated and measured BTCs of lithium for sediment V5 and V7.

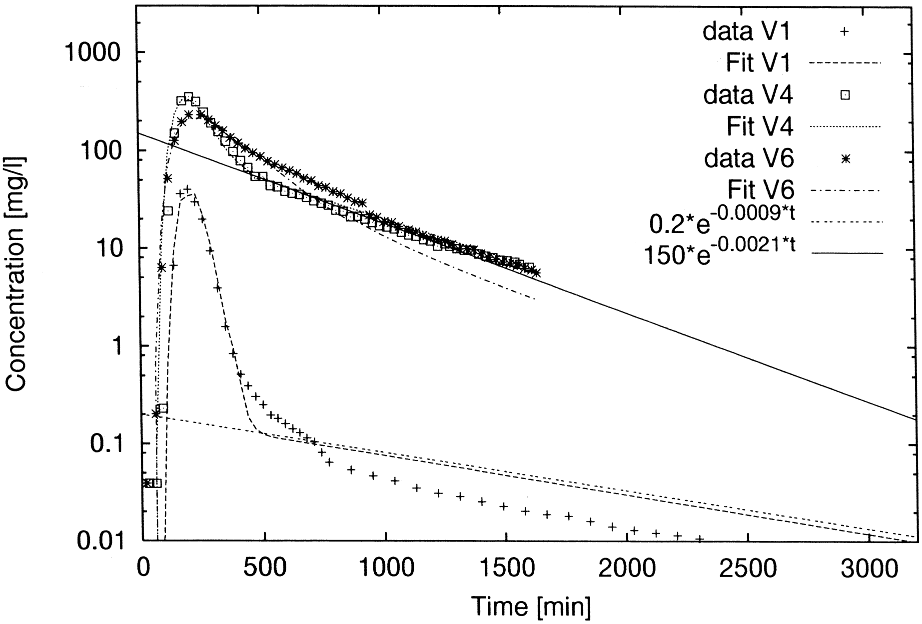

Fig. 11. Comparison of measured and fitted lithium BTCs using the two site sorption model TSEK (set 1).

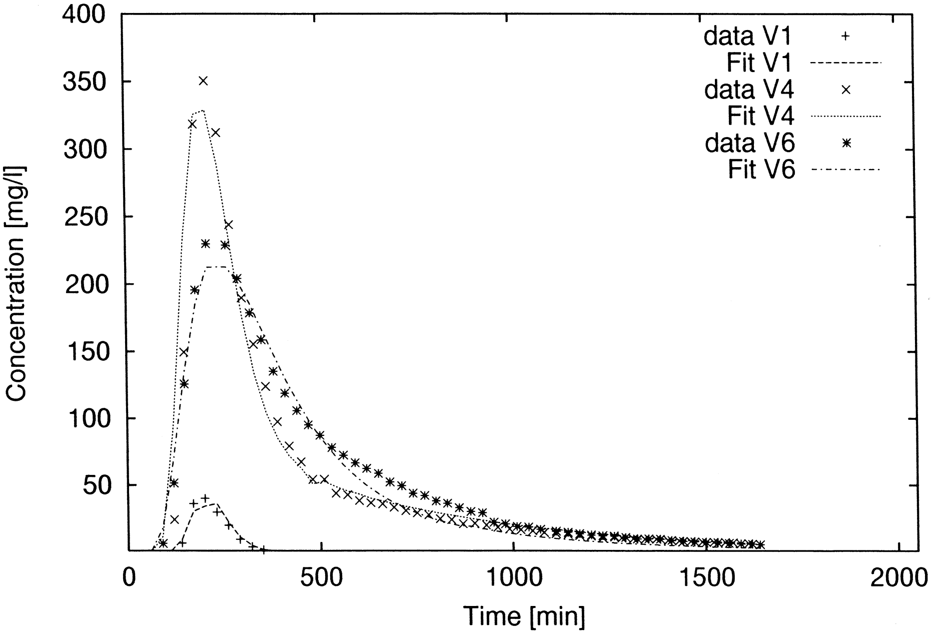

Fig. 12. Comparison of measured and fitted lithium BTCs using the two site sorption (set 1).

$\alpha = 0.0026$ min^{-1}. From the bromide BTC of sediment V4, $\theta_m/\theta = 0.73$. The mean porewater velocity and dispersion coefficient were set to $v/0.73 = 0.16$ cm min^{-1} and $D/0.73 = 0.27$ cm^2 min^{-1}. For sediment V6, $R = 2.31$, $F = 0.65$ and $\alpha = 0.0028$ min^{-1}. v and D were taken from the bromide experiment with values equal to 0.16 cm^{-1} and 0.69 cm^2 min^{-1}. Pulse duration and concentration of the pulse were taken from Table 2.

The remaining curves can be described by combining the CDE with Freundlich sorption although the agreement between measured and calculated values is not as good as for uranin. Results are shown for the BTCs obtained from sediment V5 and V7 in Fig. 10. Model calculations were done with FRETRA with $n_f = 0.6$ and $n_b = 0.5$. The values for v and D were taken from the bromide experiments. The k_f values were optimized to get the best fit.

The measured BTCs of lithium from set 2 are shown in for log-transformed concentrations in Fig. 13. The tailing of the three BTCs tends to show a linear decrease with time suggesting a linear transport operator. From asymptotic analysis, we know that in this case both transport and sorption parameter determine the long time behavior. Due to the presence of an extended tailing, the two site sorption model TSEK was used to describe the observed BTCs. The parameters R, F and α_2 were estimated by solving the equation generated by Eq. (28). For each tail of the BTCs an equation can be written in which the value of β is obtained from the slope of the tail in log representation. This results in three equations each with a different β value (Fig. 13). The resulting equation system was then solved with the fsolve routine from Maple. The use of various starting values, however, always gave negative values for the distribution coefficient k_1.

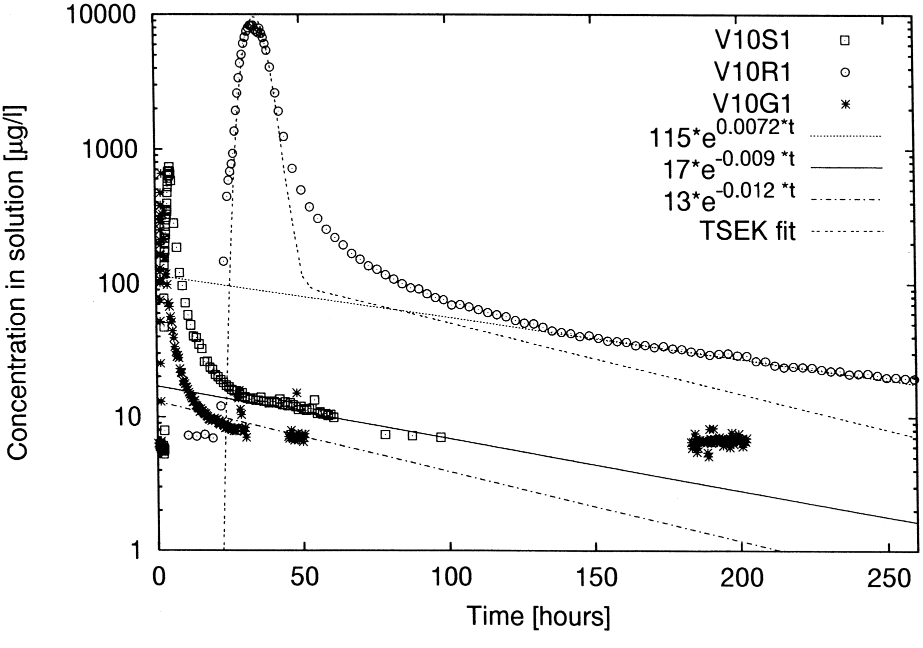

Fig. 13. Log representation of the measured lithium BTCs of set 2.

This may be attributed to two reasons. Due to the rather low solute injection concentration, the tailing was not extended enough to provide accurate estimates of the slopes. The other explanation relates to the validity of the TSEK to describe the observed BTCs. For this purpose, we used the CXTFIT software to see whether the measured BTCs could be described using the classical inverse estimate method. The TSEK was fitted to the BTC of V10R1. Initial concentration, pulse time and mean pore velocity and dispersion were fixed and only the values of R, F and α_2 were estimated to be 1.5, 0.73 and 0.0013 min^{-1} using CXTFIT by trial and error. Fig. 13 shows the fitted vs. observed BTC of V10S1 and V10G1. The calculated BTCs, however, did not describe the observed ones indicating that the TSEK was not able to describe the transport at higher velocities. No adjustment of the parameters in the TSEK could be found which was able to fit the observed behavior.

4.4. Comparison with values obtained from field scale tracer test at Krauthausen

For solute transport with Freundlich or nonlinear nonequilibrium sorption, we will assume that the large time behavior of the concentration is independent of the type of transport operator $\mathscr{L}$. This was already shown by Jaekel et al. (1996) for the case of a 1D porous medium with spatially variable dispersion coefficient. Döring et al. (1998) evaluated measured BTCs of uranin from a large scale tracer experiment at the Krauthausen field site using the fact that from asymptotic theory log–log transformed BTCs of solute undergoing Freundlich sorption should drop as $t^{-1/(1-n)}$. In this experiment bromide, uranin and lithium were used as tracers. The field site was equipped with 68 wells in order to characterize the temporal and spatial evolution of the tracers. The observation wells were equipped with multi-level-samplers having 24 sampling ports. Breakthrough curves were monitored at different depths and for more than 15 wells over a time period of 398 days for bromide and 450 days for uranin and lithium. Temporal moment analysis of the BTCs of bromide gave a mean groundwater velocity which ranged between 0.5 and 1.0 m day^{-1} (Vereecken et al., 1998a). Purpose of the experiments was to examine the role of heterogeneities on the transport of reactive solutes.

Uranin BTCs of three wells (B52, B14, B6) showing an extended tailing of the concentration values were used for asymptotic analysis. Log–log representation of these curves resulted in almost straight lines for the tailing part of the BTCs. This is depicted as an example in Fig. 14 for three BTCs observed in well B6, which is at a distance of 28 m from the injection plane. By fitting linear regression through the tailing part of the log–log transformed data, Döring et al. (1998) found that the slope of the tail remained fairly constant with depth. Assuming Freundlich sorption, the mean value for the three wells was equal to 0.58 and a variance σ^2 of 0.006. Mean value and variance of each well separately gave 0.63 ($\sigma^2 = 0.01$), 0.54 ($\sigma^2 = 0.002$), 0.58 ($\sigma^2 = 0.0008$) for B6, B14 and B52, respectively. These values are considerably lower than the batch n values which were equal to about 0.85. Using Eq. (41), the mean value of the slope α of the field BTCs is 2.38. This value is smaller than the values of the slopes obtained from sediments V3, V5 and V8 which were all equal to 3.2 but larger than the value of α for V4 which was 2.0. The latter value was explained by a nonlinear nonequilibrium

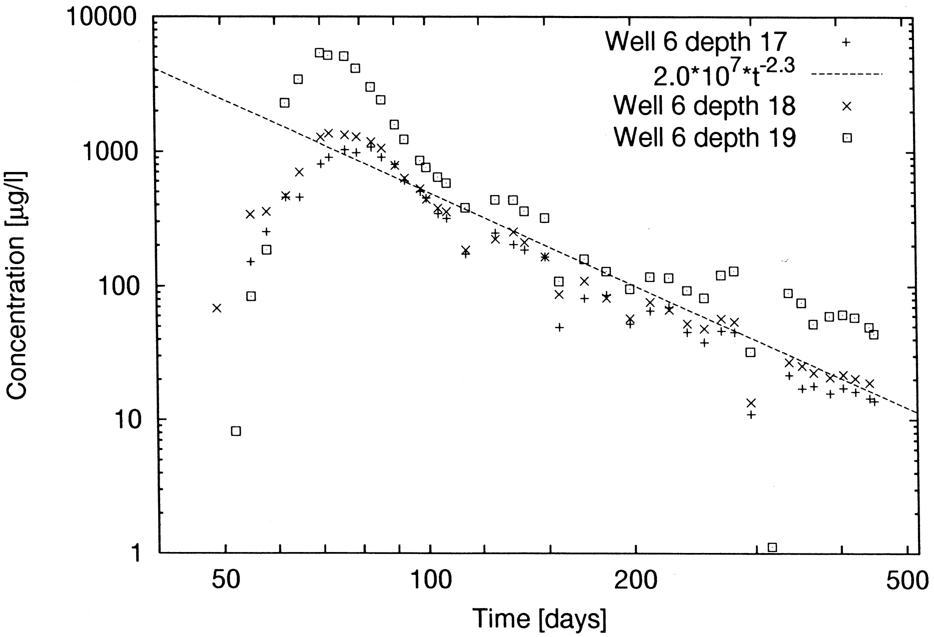

Fig. 14. Log–log representation of measured uranin BTCs at the Krauthausen field site. Measurements were performed at three different depths (depths 17, 18 and 19).

sorption process. The values of the slope from the field BTCs vary within one standard deviation between 2.0 and 2.9. This variation indicates that uranin sorption at the field site may be explained by different mechanisms. The mean α value of 2.38 suggests that nonlinear nonequilibrium sorption seems to be the dominant sorption process. However the presence of higher α values which are closer to 3.2 indicate that sorption can also be described by a Freundlich isotherm with hysteresis. It should, however be taken into account that of the eight uranin column BTCs only two showed nonequilibrium sorption of which one BTC showed the presence of nonlinearity. Additional experiments are needed to support the evidence of nonlinear nonequilibrium sorption for uranin.

5. Conclusions

Evaluation of uranin BTCs from nine sediment samples from an unconfined aquifer lead to the identification of three different sorption processes: Freundlich equilibrium sorption with hysteresis, linear nonequilibrium and nonlinear nonequilibrium sorption. The change from Freundlich equilibrium sorption to nonequilibrium conditions was found to be related to the column Peclet number. Discrimination between the different sorption mechanisms was based on asymptotic analysis of the BTCs. Freundlich n exponents from batch experiments did not provide a good description of observed uranin BTCs. The CDE with hysteretic Freundlich sorption successfully described observed

BTCs for two column experiments with uranin. The parameter values in the model were obtained from independent measurements without almost any adjustment. Only the Freundlich distribution coefficient in one of the experiment was slightly changed. Analysis of the slopes of log–log transformed field BTCs indicated that uranin sorption can be described by either hysteretic Freundlich sorption or nonlinear nonequilibrium sorption. The mean value of the slopes, however, suggest that nonlinear nonequilibrium may be the dominant process for large times. Lithium BTCs were well described by Freundlich sorption and linear kinetic sorption. Asymptotic analysis was found to be a useful tool in interpreting observed BTCs and in identifying the nature of the solute–solid interaction. Its application, however, requires the need of having extended measurements of the tail over a large time period which is not always feasible. But in view of risk assesments, ecotoxicological evaluation and sanitation strategies, correct prediction of low concentrations and their long time behavior is as important as a correct prediction of the bulk mass of contaminant.

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