Comparison of alternative models for simulating anomalous solute transport in a large heterogeneous soil column

Guangyao Gao^{a,b}, Hongbin Zhan^c, Shaoyuan Feng^{a,*}, Guanhua Huang^{a,d}, Xiaomin Mao^a

^a Center for Agricultural Water Research in China, China Agricultural University, Beijing 100083, PR China

^b State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

^c Department of Geology and Geophysics, Texas A&M University, College Station, TX 77843-3115, USA

^d Chinese–Israeli International Center for Research and Training in Agriculture, China Agricultural University, Beijing 100083, PR China

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SUMMARY

This study compared five different models for evaluating solute transport in a 1250-cm long, saturated and highly heterogeneous soil column. The five models were: the convection–dispersion equation (CDE), the mobile–immobile model (MIM), the convective lognormal transfer function model (CLT), the spatial fractional advection–dispersion equation (FADE) and the continuous time random walk model (CTRW). Each of these models was used to fit the breakthrough curve (BTC) at each distance individually and was also used to fit the BTCs at different distances simultaneously. Dependence of estimated parameters on distance was investigated. The estimated parameters at 200 cm were used to make predictions at subsequent distances. Highly anomalous transport behavior was observed in the column as the BTCs demonstrated significantly irregular shape and long tailing. This study indicated that CDE, CLT and FADE were unable to describe the anomalous BTCs adequately and their parameters changed with transport distance significantly. Compared to CDE, CLT and FADE, MIM better captured the evolution of anomalous BTCs. However, MIM did not explain the distinct BTC tailing satisfactorily. In contrast to MIM, CTRW better simulated the long tails of BTCs. The spreading parameter (β) of CTRW was close to one and remained approximately constant at different travel distances. To make the comparison of these five models more general beyond the specific transport condition in the soil column, a generic evaluation of the advantages and disadvantages of these five models was presented in terms of their theory framework and *a priori* knowledge of the model behaviors.

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Introduction

The fate and transport of solute in soils and groundwater has long been a focus of experimental and theoretical research in subsurface hydrology. An important aspect in understanding the fate of solute is to describe its transport behavior using appropriate models. The convection–dispersion equation (CDE) (Bear, 1972) is the first transport model widely used to describe solute transport in porous media. For laboratory columns packed with macroscopically homogeneous soils, it is generally accepted that solute transport can be well described by CDE. However, in heterogeneous soils the measured breakthrough curves (BTCs) usually demonstrate early arrival and distinct long tailing as a result of the inherent heterogeneity of natural soils at various scales (Berkowitz et al., 2006). These phenomena are referred to as anomalous or non-Fickian transport (Berkowitz et al., 2002), and CDE cannot de-

scribe it adequately (Levy and Berkowitz, 2003; Berkowitz et al., 2006). Such anomalous phenomena even can be found during solute transport in repacked homogeneous soil column or sandbox (e.g., Padilla et al., 1999; Levy and Berkowitz, 2003; Bromly and Hinz, 2004; Cortis and Berkowitz, 2004). Another problem of CDE is the well recognized scale-dependent dispersion, i.e., the estimated dispersion coefficient or dispersivity is not constant but rather varies with spatial and/or temporal scales (Gelhar et al., 1992). The problem of increasing dispersion coefficients is related to the lack of a macroscopic representative elementary volume in a heterogeneous field. Even if the field is macroscopically homogeneous, the dispersion coefficient is not a constant from the beginning, but only after the tracer plume has been transported over a large enough domain, containing several correlation lengths (Dentz et al., 2000). Therefore, it is often difficult for CDE with a single set of parameters to predict BTCs at different distances.

Alternative models have been proposed to account for the observed anomalous BTCs. The mobile–immobile model (MIM) presented by van Genuchten and Wierenga (1976) is a practical and physically based approach to describe anomalous solute transport

* Corresponding author. Tel.: +86 10 62736762; fax: +86 10 62736860.
E-mail address: fsy@cau.edu.cn (S. Feng).

Nomenclature

C	solute concentration [ML^{-3}]	$\bar{t}$	characteristic time in CTRW [T]
C_m	solute concentration in the mobile region [ML^{-3}]	u	laplace transfer parameter
C_{im}	solute concentration in the immobile region [ML^{-3}]	v	pore-water velocity [LT^{-1}]
C_0	constant source concentration [ML^{-3}]	v_m	mobile pore-water velocity [LT^{-1}]
D	dispersion coefficient in CDE [L^2T^{-1}] and FADE [$\text{L}^\varphi\text{T}^{-1}$]	v_ψ	particle transport velocity [LT^{-1}]
D_m	dispersion coefficient in the mobile region [L^2T^{-1}]	x	distance [L]
D_ψ	generalized dispersion coefficient in CTRW [L^2T^{-1}]	θ	total water content
l	reference distance in CLT [L]	θ_m	water content in the mobile region
n	porosity of porous media	θ_{im}	water content in the immobile region
q	flow rate [LT^{-1}]	ϕ	mobile water fraction
t	time [T]	ω	mass transfer coefficient [T^{-1}]
t_1	lower limit time when the power law behavior begins in CTRW [T]	μ_l	mean of $\ln(t)$ at l in CLT
t_2	cut-off time from power law behavior to exponential decay in CTRW [T]	σ_l	standard deviation of $\ln(t)$ at l in CLT
		φ	order of fractional differentiation
		γ	skewness of transport process

behavior in heterogeneous soils. The MIM assumes that the anomalous transport is caused by immobile or stagnant water in the soil system (e.g., van Genuchten and Wierenga, 1977; Bond and Wierenga, 1990; Griffioen et al., 1998; Toride et al., 2003; Haggerty et al., 2004). The MIM is different from CDE in that it separates the liquid regime into mobile (flowing) and immobile (stagnant) regions with solute transfer between these two regions, accounting for early arrival and long time tailing of solute transport (van Genuchten and Wierenga, 1976; Toride et al., 1999). As pointed out by Griffioen et al. (1998), a major attribute of MIM is that it characterizes, in simple mathematical forms, the observed anomalous BTCs and the influence of soil's heterogeneous structure on transport process. It has been shown that the MIM can successfully describe solute transport in homogeneous repacked soil (Bond and Wierenga, 1990; Padilla et al., 1999; Toride et al., 2003), aggregated soil (van Genuchten and Wierenga, 1977; Nkedi-Kizza et al., 1983; Brusseau et al., 1994), undisturbed field soil cores (Smettem, 1984), and locally stratified soil (Herr et al., 1989; Li et al., 1994).

Jury (1982) and Jury and Roth (1990) applied the concept of a transfer function to model solute transport in complex soil systems. The transfer function model treats the soil as a black box and characterizes the output as a linear function of the input. The transfer function models are used based on a probability density function (pdf) of the travel time of solute particles reaching a certain distance. Among the transfer function models, the most widely used is the convective lognormal transfer function model (CLT) in which the pdf is assumed to be lognormal. Whereas CDE assumes complete lateral mixing of solutes during transport, the CLT neglects the lateral mixing (Bromly and Hinz, 2004). The CLT has been successfully applied to both laboratory columns (e.g., Zhang et al., 1994; Vanderborght et al., 1996, 1997; Bromly and Hinz, 2004) and field tracer tests (e.g., Jury and Roth, 1990).

Recently, Benson et al. (2000a,b) proposed the spatial fractional advection–dispersion equation (FADE) to describe anomalous transport and applied it to solute transport at the Cape Cod site (Benson et al., 2000b) and MADE site (Benson et al., 2001). The basic idea of FADE is that solute particles undergo Lévy motion, in contrast to Brownian motion which is the basis for CDE. In FADE, the dispersion flux is proportional to the fractional derivative of solute concentration rather than integer derivative assumed in CDE. The effect of heterogeneity and scaling behavior of the solute plume are reflected by the exponent of the fractional derivative (Benson et al., 2000a,b). The FADE has been used to simulate solute

transport through unsaturated soils (Pachepsky et al., 2000), saturated soils (Huang et al., 2006), streams and rivers (Zhang et al., 2005), and overland flow (Deng et al., 2006).

Another alternative model is the continuous time random walk (CTRW) theory applied by Berkowitz et al. (2006) to describe anomalous transport in porous and fractured media. The CTRW visualizes solute transport in a variable velocity field as a series of particle jumps or transitions via different paths with spatially changing velocities, and it allows waiting between jumps (Berkowitz et al., 2006). This kind of transport can in general be represented by a joint probability density function $\psi(s,t)$, which describes each particle transition over a distance and direction s in time t (Berkowitz et al., 2006). The CTRW has been used to quantify laboratory tracer tests (Berkowitz et al., 2000, 2008; Levy and Berkowitz, 2003; Bromly and Hinz, 2004; Cortis and Berkowitz, 2004; Cortis et al., 2006; Xiong et al., 2006; Berkowitz and Scher, 2008) and field tracer migration (Berkowitz and Scher, 1997, 1998; Berkowitz et al., 2008).

It is generally proven that MIM, CLT, FADE and CTRW and their modified forms are more suitable to describe anomalous solute transport in heterogeneous soils than CDE. There are a few studies about comparison between these five models. For example, Bromly and Hinz (2004) compared the performance of CDE, MIM, CLT and CTRW for describing anomalous transport in homogeneous unsaturated repacked sand, and indicated that CLT and CTRW better captured solute transport behavior. However, to our knowledge, less attention has been paid to compare these five models for describing solute transport in heterogeneous soils. Furthermore, as pointed out by Padilla et al. (1999), Bromly and Hinz (2004), it is important to study the evolution of solute spreading with distance at relatively large scale, and the performance of a model should be verified across a range of travel distances. However, most of the previous studies in laboratory scale were focused on solute transport through relatively short columns. Therefore, it is worthwhile to evaluate the performance of these five models for describing solute transport through relatively large heterogeneous soil domain under controlled experimental conditions.

The objectives of this work are to compare the performances of CDE, MIM, CLT, FADE and CTRW for describing conservative solute transport process through a large heterogeneous soil column used in a controlled experiment conducted by Huang et al. (1995), and to generally evaluate these five models in terms of their reliability and limitations for describing solute transport behaviors in heterogeneous soils.

Solute transport theory

CDE

The CDE for one-dimensional transport of a non-reactive solute during steady water flow is written as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

where C is the solute concentration (ML^{-3}); D is the hydrodynamic dispersion coefficient (L^2T^{-1}); v is the average pore-water velocity (LT^{-1}); x is the distance (L); and t is the time (T).

For an initially solute-free and semi-finite system, the analytical solution of CDE subject to the third-type or flux-type inlet boundary condition (constant mass flux at inlet) is (Parker and van Genuchten, 1984, see Eqs. (7) and (9)):

$$C(x, t) = \frac{C_0}{2} \left[\operatorname{erfc}\left(\frac{x - vt}{2\sqrt{Dt}}\right) + 2\sqrt{\frac{v^2 t}{\pi D}} \exp\left(-\frac{(x - vt)^2}{4Dt}\right) - \left(1 + \frac{vx}{D} + \frac{v^2 t}{D}\right) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x + vt}{2\sqrt{Dt}}\right) \right] \quad (2)$$

where C_0 is the constant source concentration (ML^{-3}) and $\operatorname{erfc}()$ is the complementary error function.

When CDE is used to describe solute transport in a heterogeneous medium, the macrodispersion is used presuming that the heterogeneous permeability field is macroscopically homogeneous. Once the tracer plume has travelled long enough and sampled enough of the heterogeneity, the mixing over different streamlines results in macrodispersion with a constant coefficient, which is proportional to the integral scale of the field. Before this asymptotic limit is reached, the dispersion coefficient is time-dependent (Dentz et al., 2000). Such a time-dependent dispersion coefficient was not considered in this study.

MIM

The MIM consists of a conventional convection–dispersion equation for solute transport in the mobile region, coupled with a term which describes mass transfer of solute between mobile and immobile regions. The second equation expresses the solute mass transfer flux as being proportional to the concentration difference between these two regions. The one-dimensional MIM for a conservative solute transport during steady water flow is given by (van Genuchten and Wierenga, 1976):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \quad (3)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im}) \quad (4)$$

where θ_m and θ_{im} are the water contents in the mobile and immobile liquid regions, respectively, and $\theta_m + \theta_{im} = \theta$; θ is the total water content, and for saturated flow θ equals to the porosity; C_m and C_{im} are the solute concentrations in the mobile and immobile liquid regions (ML^{-3}), respectively; D_m is the hydrodynamic dispersion coefficient in the mobile region (L^2T^{-1}); v_m is the mobile pore-water velocity (LT^{-1}) and $\theta_m v_m$ is equal to the measured Darcy velocity q (LT^{-1}); ω is the mass transfer coefficient (T^{-1}).

With the initial condition of zero concentration and third-type inlet boundary condition, the analytical solutions of MIM for a semi-infinite system in Laplace domain are (Toride et al., 1999):

$$\bar{C}_m(x, u) = \frac{2C_0}{u + u\sqrt{1 + 4D_m\xi/v_m}} \exp\left(\frac{v_m - \sqrt{v_m^2 + 4D_m\xi}}{2D_m} x\right) \quad (5)$$

$$\bar{C}_{im}(x, u) = \frac{2\omega C_0}{(\omega + u\theta_{im})(u + u\sqrt{1 + 4D_m\xi/v_m})} \times \exp\left(\frac{v_m - \sqrt{v_m^2 + 4D_m\xi}}{2D_m} x\right) \quad (6)$$

where $\xi = \left[\frac{\omega\theta_{im}}{\theta_m(\omega + u\theta_{im})} + 1\right]u$ and u is the Laplace variable. To obtain the actual time domain solutions, the Laplace solutions can be inverted analytically (Toride et al., 1999) or numerically based on the de Hoog algorithm (de Hoog et al., 1982).

The MIM described above uses a lumped single first-order rate to describe the complex mass transfer process for the sake of simplicity. However, for natural soils or complex and heterogeneous aquifers, as a result of small-scale variations in porous media properties, the rates and types of mass transfer vary greatly (Haggerty and Gorelick, 1995). The presence of multiple timescales of mass transfer has been reported by Haggerty et al. (2004) who found that the estimated mass transfer timescale for single-rate mobile–immobile transport was better correlated to the experimental duration and solute residence time than to velocity. To account for multiple and simultaneous mass transfer processes, Haggerty and Gorelick (1995) developed a multiple-rate MIM model using a distribution of mass transfer coefficients coupled to the convection–dispersion solute transport model. The single-rate MIM and the diffusion models for different geometries are all shown to be the special cases of the multiple-rate MIM model (Haggerty and Gorelick, 1995; Carrera et al., 1998; Haggerty et al., 2000; Dentz and Berkowitz, 2003). In this work, “MIM” is used to denote the single-rate mobile–immobile model, and “MRMT” is used to denote the multiple-rate MIM transport model. The MRMT model has been applied in the laboratory soil column experiments (Haggerty and Gorelick, 1998) and field tracer tests (Haggerty et al., 2000).

CLT

The CLT model assumes that solute moves by convection at different velocities in individual flow tubes without mixing between adjacent tubes. In this way, the travel time probability density function (pdf) at an arbitrary distance x for flux concentrations, denoted as $f^f(x, t)$, can be derived from the pdf at the reference distance l as (Jury and Roth, 1990):

$$f^f(x, t) = (l/x)f^f(l, tl/x) \quad (7)$$

Eq. (7) means that the probability density of tracer reaching distance x after time t is equal to the probability density of reaching the reference distance l after time tl/x (Bromly and Hinz, 2004). Such an assumption is necessary for CLT to make predictions at any given distance. For the CLT model, the travel time pdf is assumed to be a lognormal density function (Jury, 1982):

$$f^f(l, t) = \frac{1}{\sqrt{2\pi}\sigma_l t} \exp\left[-\frac{(\ln(t) - \mu_l)^2}{2\sigma_l^2}\right] \quad (8)$$

where μ_l and σ_l are the mean and standard deviation of $\ln(t)$ at the reference distance l , respectively. With Eqs. (7) and (8), the travel time pdf at distance x can be expressed as:

$$f^f(x, t) = \frac{1}{\sqrt{2\pi}\sigma_x t} \exp\left[-\frac{(\ln(tl/x) - \mu_l)^2}{2\sigma_l^2}\right] \quad (9)$$

From Eq. (9), it can be found that the travel time pdf at x also obeys lognormal distribution with $\mu_x = \mu_l + \ln(x/l)$ and $\sigma_x = \sigma_l$, where μ_x and σ_x are the mean and standard deviation of $\ln(t)$ at distance x ,

respectively. As the CLT model assumes a linear transport process, the flux concentration resulting from a step input of solute is essentially equal to the time integration of the travel time pdf (Jury and Roth, 1990; Vanderborght et al., 1997):

$$C^f(x, t) = \frac{C_0}{2} \left\{ 1 + \operatorname{erf} \left[\frac{\ln(tl/x) - \mu_l}{\sqrt{2}\sigma_l} \right] \right\} \quad (10)$$

where C^f is the flux concentration and $\operatorname{erf}()$ is the error function. Parker and van Genuchten (1984) have discussed the relationship between the flux concentration and resident concentration which is used in above CDE and MIM models. For CLT model, Vanderborght et al. (1996, 1997) have given the equivalent resident concentration for a step input as:

$$C^r(x, t) = \frac{C_0}{2} \left\{ 1 + \operatorname{erf} \left[\frac{\ln(tl/x) - \mu_l - \sigma_l^2}{\sqrt{2}\sigma_l} \right] \right\} \quad (11)$$

where C^r is the resident concentration.

FADE

The spatial FADE assumes that movement of solute particles follows the Lévy motion and the associated transition probability is described by the standard symmetric Lévy probability distribution function (Benson et al., 2000a,b). Benson et al. (2000a,b) derived the one-dimensional spatial FADE for a non-reactive solute from the Fokker–Plank equation (FPE):

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + \left(\frac{1}{2} + \frac{\gamma}{2} \right) D \frac{\partial^\varphi C}{\partial x^\varphi} + \left(\frac{1}{2} - \frac{\gamma}{2} \right) D \frac{\partial^\varphi C}{\partial (-x)^\varphi} \quad (12)$$

where D is the dispersion coefficient with dimension of $[L^\varphi T^{-1}]$, φ is the order of fractional differentiation and $1 < \varphi \leq 2$. φ reflects the tailing of the Lévy probability distribution. As φ decreases from 2, the Lévy distribution deviates more from the Gaussian distribution and the tail of the Lévy distribution becomes heavier. When $\varphi = 2$, the Lévy distribution converges to the Gaussian distribution and FADE reduces to CDE. γ ($-1 \leq \gamma \leq 1$) is the skewness of transport, which describes the bias of dispersion. γ reflects the relative weight of solute particle forward versus backward transition probability. For $-1 \leq \gamma \leq 0$, the transition probability and dispersion is skewed backward describing a slowly evolving contaminant plume, while for $0 \leq \gamma \leq 1$ the transition probability and dispersion is skewed forward describing a fast evolving contaminant plume. When γ equals to 0, the transition of solute particles and dispersion in FADE is symmetric. This symmetrical FADE was used in this study.

For a semi-infinite system initially free of solute and a step input at $x = 0$ with concentration of C_0 , the analytical solution of the symmetrical FADE can be expressed as (Pachepsky et al., 2000; Huang et al., 2006):

$$C(x, t) = C_0 \left[1 - F_\varphi \left(\frac{x - vt}{(|\cos(\pi\varphi/2)|Dt)^{1/\varphi}} \right) \right] \quad (13)$$

where $F_\varphi(y)$ is the symmetric φ -stable probability function (Pachepsky et al., 2000):

$$F_\varphi(y) = C(\varphi) + \frac{\operatorname{sign}(1 - \varphi)}{2} \int_0^1 \exp \left(-y^{1-\varphi} U_\varphi(\chi) \right) d\chi \quad (14)$$

where χ is the integration variable, $C(\varphi)$ and $U_\varphi(\chi)$ can be expressed as (Pachepsky et al., 2000):

$$C(\varphi) = \begin{cases} 1 & \varphi > 1 \\ \frac{1}{2} & \varphi < 1 \end{cases} \quad \text{and} \quad U_\varphi(\chi) = \left[\frac{\sin(\pi\varphi/2)}{\cos(\pi\varphi/2)} \right]^{\frac{\varphi}{1-\varphi}} \quad (15)$$

CTRW

The CTRW model simulates the movement of solute particles by the joint probability density function $\psi(s, t)$ that considers how far

the particles can jump and how long the particles are trapped between two successive jumps. $\psi(s, t)dsdt$ is the probability that a particle jumps with a length between s and $s + ds$ and at the same time is trapped for a time between t and $t + dt$, where ds and dt are the spatial and temporal intervals, respectively. For most practical applications, the joint distribution can be decoupled into the product of the marginal density distributions. In this situation, $\psi(s, t)$ can be expressed as $\psi(s, t) \approx p(s)\psi(t)$, where $p(s)$ denotes the transition length probability density function and $\psi(t)$ denotes the transition-time distribution function (Berkowitz et al., 2002). When $p(s)$ can be assumed to be Gaussian, the one-dimensional CTRW model in Laplace domain can be written as follows (Dentz et al., 2004; Cortis and Berkowitz, 2004):

$$u\bar{C}(x, u) - C_i(x) = -\bar{M}(u) \left[v_\psi \frac{\partial}{\partial x} \bar{C}(x, u) - D_\psi \frac{\partial^2}{\partial x^2} \bar{C}(x, u) \right] \quad (16)$$

where u is the Laplace variable, C_i is the initial concentration, v_ψ and D_ψ are the transport velocity and generalized dispersion coefficient, respectively, and $\bar{M}(u)$ is the memory function. It is important to recognize that the transport velocity, v_ψ , is distinct from the average pore velocity, v , while in CDE, these velocities are identical. Similarly, the dispersion coefficient, D_ψ , has a different physical interpretation from the hydrodynamic dispersion coefficient in CDE. In Eq. (16), $\bar{M}(u)$ is expressed as:

$$\bar{M}(u) = \bar{t} u \frac{\bar{\psi}(u)}{1 - \bar{\psi}(u)} \quad (17)$$

where $\bar{t}$ is some characteristic time and $\bar{\psi}(u)$ is the Laplace transform of $\psi(t)$. $\bar{M}(u)$ captures the anomalous transport induced by the small- and intermediate-scale unresolved heterogeneities. It also reflects the non-local behavior of the transport, which is caused by stagnation zones. v_ψ is used to account for large-scale heterogeneities, while D_ψ describes local dispersion (Dentz et al., 2004).

The transition-time distribution function $\psi(t)$ characterizes the nature of solute transport and can adopt many choices (Berkowitz et al., 2006). In this study, we used the truncated power-law distribution function whose Laplace transform is given by (Dentz et al., 2004):

$$\bar{\psi}(u) = (1 + \tau_2 u t_1)^\beta \exp(t_1 u) \Gamma(-\beta, \tau_2^{-1} + t_1 u) / \Gamma(-\beta, \tau_2^{-1}) \quad (18)$$

where $\tau_2 = t_2/t_1$ and $\Gamma(a, x)$ is the incomplete Gamma function. The time t_1 represents the approximate median transition time and sets the lower limit from which the power law behavior begins, so that the time range of interest is $t > t_1$. The time t_2 governs the crossover from power law to exponential decay. For transition times $t_1 \leq t \leq t_2$, $\psi(t)$ behaves according to a pure power law, while for $t \geq t_2$, $\psi(t)$ decreases exponentially. Therefore, the truncated power-law transition-time distribution function is a simple and general form of $\psi(t)$ allowing for a power law decay to evolve to an exponential decay (Dentz et al., 2004).

The memory function $\bar{M}(u)$ is determined by substitution of Eq. (18) into Eq. (17) with $\bar{t} = t_1$. When using the truncated power-law transition-time distribution function, the very nature of solute transport can be characterized by the value of constant exponent β which falls into three possible ranges: $0 < \beta < 1$, $1 < \beta < 2$ and $\beta > 2$. The case of $0 < \beta < 1$ describes the most anomalous transport where both the mean and standard deviation of tracer plume scale as power laws with time. For $1 < \beta < 2$, solute transport is anomalous where the plume velocity is constant in time and the standard deviation retains the power law scaling. When $\beta > 2$, solute transport is Fickian and CTRW is equivalent to CDE.

For a unit steady state third-type boundary condition at the inlet, the analytical solution of CTRW is (Cortis and Berkowitz, 2004):

$$\bar{C}(x, u) = \frac{1}{u} \times \frac{(w+1)\exp(k) + (w-1)\exp(z)}{[(w+1)\bar{M}v_\psi + 2u\alpha_\psi]\exp(w/\alpha_\psi) + [(w-1)\bar{M}v_\psi - 2u\alpha_\psi]} \quad (19)$$

where $w = \sqrt{1 + \frac{4u\alpha_\psi}{\bar{M}v_\psi}}$, $z = \frac{(1+w)x}{2\alpha_\psi}$, $k = \frac{2w-xw-x}{2\alpha_\psi}$ and $\alpha_\psi = \frac{D_\psi}{v_\psi}$. The concentrations in time domain can be obtained by the de Hoog algorithm for numerical Laplace inverse transform (de Hoog et al., 1982).

It has been claimed that the CTRW approach is a general framework for dealing with Fickian and anomalous transport as it includes the classical CDE, the single-rate and multiple-rate MIM model, and spatial FADE (Berkowitz et al., 2006). Dentz and Berkowitz (2003) have shown that the MRMT model is formally identical to CTRW when the transition length and waiting time distributions decouple, and CTRW and MRMT yield the same transport behavior if their memory functions are identical. When the transition length can be approximated as a Lévy flight and its probability density function has a power law tail, the CTRW reduces to the spatial FADE (Zhang et al., 2005).

Materials and methods

Large column experiment

Huang et al. (1995) conducted a laboratory tracer transport experiment in a 1250-cm long, horizontally placed heterogeneous soil column with cross-section areas of $10 \times 10 \text{ cm}^2$ during steady saturated flow to investigate the scale effect of solute transport in heterogeneous soils. As far as we know, the heterogeneous column in this experiment is one of the longest soil columns used for investigating solute transport in laboratory scales. There exist some other solute tracer experiments on large lab scales. For example, Jose et al. (2004) performed a conservative tracer test in a 14-m-long sandbox.

The heterogeneous soil column was packed with a wide range of soil materials including clay, fine-, medium- and coarse-textured sands, gravel, and pebbles of 1–2 cm in diameter, as well as mixed formations of these materials with various shapes and sizes. A relatively high degree of heterogeneity was formed by rather arbitrarily embedding several lenses and layers with different shapes and sizes into the heterogeneous column. The soil materials were taken from the deposits of a mountain river. They were clean, well-sorted and contained negligible organic matter. On average, the particle size of the heterogeneous soil column decreased gradually from very coarse at the inflow end to relatively fine at the outlet. The soil column was saturated slowly with distilled water, and the steady-state water flow condition was established by using Mariotte bottles at the inlet position and constant head level apparatus at the outlet position. The sodium chloride (NaCl) solution with a concentration of $C_0 = 6 \text{ g/L}$ as the tracer was injected into the column with step input. The porosity for the column (n) was estimated to be about 0.37 (Huang et al., 1995). The flow rate (q) calculated by the observed constant drainage rate at the outlet of the column was 0.239 cm/min. Therefore, the average pore-water velocity measured by Huang et al. (1995) is 0.646 cm/min ($=q/n$). Concentrations of the tracer NaCl during the experiment were measured with twelve electrical conductivity probes inserted laterally in the column with 100-cm intervals. One BTC was obtained from each of those twelve probes after the experiment. More detailed information about this experiment can be found from Huang et al. (1995).

With respect to this experiment, several additional points need to be mentioned. First, this experiment tried to mimic the field-

scale transport as it produced similar heterogeneous structure to those found in natural soils, i.e., various types of locally heterogeneities embedded in many types of soil materials. Second, the lateral dimension of the column is very small in contrast to its length and solute transport can be considered as a one-dimensional problem. This implies that lateral water flow that funnels the water flow into preferential flow paths is hampered. Such funneling processes are very important for field-scale transport processes. Third, there is a possibility that the soil chemistry may be altered during the soil saturation process as the diffuse double layers and adsorbed cations of the soils could be disturbed by the distilled water. Clay particles may also be dispersed during the saturation process. Meanwhile, the use of sodium chloride as a tracer might lead to some degree of clay dispersion, which may lead to clogging of some pores. Such possible change of the soil structure does not affect the essence of this study since there is no attempt to obtain detailed soil information to interpret the BTCs. In addition, there is no observable change of soil structure during the experiment.

Parameter estimation and simulation

As the properties of soil materials in the column change systematically with distance, the domain is actually non-stationary. It has been claimed that sophisticated approaches such as the stochastic-analytic approaches (Neuman and Tartakovsky, 2008) and the developed models of Zhang et al. (2007a), Cortis et al. (2004) can account for solute transport in non-stationary media. However, to account explicitly for non-stationary media, detailed information about the spatial distribution of hydraulic properties should be needed. Such information is impractical to obtain for most field-scale transport problems (Sudicky and Huyakron, 1991), and in this study only breakthrough curves and steady flow rates were measured. In addition, these approaches inevitably introduce more parameters. In order to evaluate large-scale transport behavior without detailed information of the hydraulic property distribution inside the soil column, we applied the macroscopic mean transport equation with effective parameters as in the stochastic approach. This means that CDE, MIM, CLT, FADE and CTRW with effective parameters and mean concentrations are used to analyze the observed BTCs at different distances. In this way, the estimated parameter at a certain measured point represents the average value pertaining to the applicable travel distance between the inlet position and the measured point. The spatial distribution of the resulting parameters can approximately reflect the solute transport evolution with distance in the heterogeneous soil column (Huang et al., 1995).

In the simulation process, the BTC at each distance was first fitted with CDE, MIM, CLT, FADE and CTRW, respectively. After that, multiple BTCs at different distances were simultaneously fitted to each of the five models. It should be noticed that in the simultaneous fitting process, the BTC at 100 cm was excluded as homogeneous coarse medium was used in the first 100 cm of the column. The dependence of the estimated model parameters on distance was also investigated. Finally, the estimated parameters at 200 cm were used to predict the BTCs at subsequent distances.

The software CXTFIT2.1 (Toride et al., 1999) was used to fit the observed BTCs with CDE and MIM. Two parameters (v , D) in CDE and three parameters in MIM (ϕ , D_m and ω) were estimated, respectively, where ϕ denotes the mobile water fraction ($\phi = \theta_m/\theta$). As the flow rate (q) and porosity of the column (n) were prescribed in the experiment, the mobile pore-water velocity (v_m) in MIM can be determined with the fitted ϕ value ($v_m = q/\theta_m = q/(\phi n)$). In CLT, the reference distance was set at 200 cm. The Levenberg–Marquardt nonlinear least-square optimization approach was used to find μ_i and σ_i . For FADE, the FADE Main Fortran code (Huang et al., 2006) was used to simulate the BTCs and three parameters (v , D and φ)

were estimated. The CTRW model was implemented by the CTRW MATLAB toolbox (<http://www.weizmann.ac.il/ESER/People/Brian/CTRW/>). Five parameters (v_{ψ} , D_{ψ} , β , t_1 , and t_2) were fitted for CTRW.

To compare all the models considered, both the determination coefficient (r^2) and root mean square error (RMSE) were used as two criteria to reflect the goodness of simulation, which can be expressed as:

$$r^2 = 1 - \frac{\sum_{i=1}^N (C_{io} - C_{ie})^2}{\sum_{i=1}^N (C_{io} - \bar{C}_{io})^2} \quad (20)$$

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (C_{io} - C_{ie})^2} \quad (21)$$

where C_{ie} is the estimated concentration, C_{io} is the observed concentration, $\bar{C}_{io}$ represents the mean values of C_{io} , and N is the number of observed concentration data at a particular observation point.

Results and discussion

Comparison of fitting results of five models

Fig. 1 shows the measured and fitted BTCs at distances of 100 cm, 400 cm, 600 cm, 800 cm and 1000 cm. The BTC at each distance was individually fitted with CDE, MIM, CLT, FADE and CTRW. The concentration data in the figure were normalized by the input constant concentration (C_0). The estimated parameters and associated values of r^2 and RMSE are listed in Table 1 for CDE and MIM and in Table 2 for CLT, FADE and CTRW. In Fig. 1, the fitting results of CLT are not represented as CLT has nearly the same fitting results as CDE. This is also reflected in Tables 1 and 2 which show that CDE and CLT give nearly the same values of r^2 and RMSE. This result is consistent with the study of Jury and Roth (1990) who indicated that CLT was virtually indistinguishable from CDE when they were used to fit data at a given distance.

The observed BTC at 100 cm shows a relatively regular and sigmoidal shape, and the simulation results of CDE, MIM, CLT and CTRW are nearly indistinguishable and in excellent agreement with the measured concentrations, as shown in Fig. 1A. The r^2 and RMSE values of CDE, MIM, CLT and CTRW are nearly equal to each other (0.986 and 0.046, respectively), as shown in Tables 1 and 2. This result is attributable to the fact that the material packed in the first 100 cm of the column is homogeneous coarse medium (Huang et al., 1995). As shown in Table 1, the estimated value of mass transfer coefficient of MIM at the distance of 100 cm is nearly equal to zero ($\omega \rightarrow 0$), and MIM reduces to CDE in this extreme case. When the BTC at 100 cm is fitted with CTRW, the t_2 value is 0.0297 min, which is much smaller than the time range of the BTC. This result indicates that solute transport has translated to Fickian and CTRW is equivalent to CDE (Berkowitz et al., 2006).

As shown in Fig. 1B–E the measured BTCs at distances of 400 cm, 600 cm, 800 cm and 1000 cm are much irregular and asymmetric. The measured maximal normalized concentrations are all less than 1 within the experimental time period because of distinct tailing at later times, indicating anomalous transport in scales greater than 100 cm. This result is expected owing to the texturally non-homogeneous nature of soils both along and perpendicular to the flow direction in the column (Huang et al., 1995).

In Fig. 1B–C, there are profound discrepancies between the measured BTCs at 400 cm or 600 cm and those fitted by CDE, CLT and FADE. Not only the overall shapes of CDE, CLT and FADE fitted curves are not similar to the measured BTCs, but the measured concentrations are much lower than those simulated by CDE, CLT and FADE at the tails of BTCs. Compared to CDE and CLT, FADE provides somewhat better simulation results at the tailing parts of BTCs, as evident from Fig. 1B–C. This indicates that FADE is capable

of describing the long tail of BTCs to some extent, which has also been reported by Benson et al. (2000a,b).

With respect to the BTCs at 400 cm and 600 cm, the observed BTCs at distances of 800 cm and 1000 cm exhibit relatively regular shape, as shown in Fig. 1D–E. The simulation results of CDE, CLT and FADE are all close to the measured data at distances of 800 cm and 1000 cm. However, the measured BTCs still demonstrate tailing to some extent, whereas CDE, CLT and FADE are unable to account for it adequately, as evident from Fig. 1D–E.

As shown in Fig. 1B–E, compared to CDE, CLT and FADE, both MIM and CTRW better capture the evolution of the measured BTCs at distances of 400 cm, 600 cm, 800 cm and 1000 cm, especially their early stage and long tailing parts. The better performance of MIM and CTRW is also reflected by the greater r^2 values and much smaller RMSE values, as evident from Tables 1 and 2. However, the fitting results of MIM at the tails of BTCs are slightly smaller than the measured results. These discrepancies are significant at 400 cm and 600 cm with respect to those at 800 cm and 1000 cm when comparing Fig. 1B–C with Fig. 1D–E. Compared to MIM, CTRW provides excellent fitting results to the tails of BTCs.

After fitting the BTCs at individual distances separately, we then try to fit the BTCs at all distances except the one at 100 cm simultaneously to see if the models can describe the BTCs with a single set of parameters. Fig. 2 shows the simulated solute concentrations at distances of 400 cm, 600 cm, 800 cm and 1000 cm. The values of estimated parameters, r^2 and RMSE are listed in the last row of Tables 1 and 2. As expected, the simultaneously fitted BTCs do not describe the observed data at each distance as well as the individually fitted curves when comparing Fig. 1 with Fig. 2. The poor performance of simultaneous fits is also indicated by the smaller r^2 and larger RMSE values of simultaneous fits than those of individual fits, as shown in Tables 1 and 2.

In Fig. 2, CDE and CLT provide different simultaneous fitting results. The performance of simultaneous fits of CLT is somewhat better than that of CDE, indicated by the larger r^2 and smaller RMSE values of CLT as shown in Tables 1 and 2. This result is due to that although CLT and CDE can describe data at one distance equally, they will diverge rapidly with distances. Similar conclusion has also been reported by Jury and Roth (1990). From Fig. 2, it is evident that CDE, CLT and FADE are difficult to describe BTCs in the heterogeneous column with only one set of parameters. Compared to CDE, CLT and FADE, MIM provides better simultaneous fits as evident from Fig. 2. However, at late times of BTCs, the fitting results of MIM are remarkably smaller than the observed solute concentrations. As shown in Fig. 2, the simultaneous fitting results of CTRW are generally in agreement with the measured data except some discrepancies during the early times at 400 cm and the intermediate times at 600 cm. This finding indicates the applicability of CTRW to capture the BTCs at different distances with a single set of parameters. It is notable that CTRW provides much better simultaneous fitting results at the tails of BTCs with respect to MIM.

Interpretation of estimated model parameters

It is expected that the fitted parameter field of each model has a trend as a result of the specific heterogeneous structure in the soil column. In this subsection, the changing patterns of fitting parameters were thoroughly interpreted, which had two expected implications. First, the variation of model parameters can reflect solute transport properties in an approximate manner. Second, the dependence of parameters on distance is also an indication of applicability of the model in describing solute transport across a range of distances, which is very important to evaluate a model (Bromly and Hinz, 2004).

As shown in Table 1, the fitting velocity values of CDE are within the range of 0.817–1.153 cm/min and vary dramatically with dis-

Fig. 1. The breakthrough curve at each distance was individually fitted using each of the five models (CDE, MIM, CLT, FADE and CTRW). Examples of fitting results at distances of (A) 100 cm, (B) 400 cm, (C) 600 cm, (D) 800 cm, and (E) 1000 cm are shown, respectively. The fitting results of CLT are not represented as they are nearly indistinguishable from those of CDE.

tance. This velocity range agrees well with the result (0.828–1.157 cm/min) estimated by Huang et al. (1995). The variation of velocity values is a result of the heterogeneous nature of the soil column. The dispersion coefficients of CDE tend to increase with distance from 100 cm to 700 cm. For distances greater than 800 cm, the dispersion coefficient fluctuates around $100 \text{ cm}^2/\text{min}$. The maximal value of dispersion coefficient at 700 cm appears to be the result of heterogeneities in the form of nearly horizontal

lenses which enhances solute spreading around this distance (Huang et al., 1995). Huang et al. (1995) found that the dispersivity value for the column varied between 3 and 130 cm, and ascribed such a variation to the particular makeup of heterogeneities in the column. This distance-dependent dispersion coefficient indicates that CDE cannot provide an appropriate description for the evolution of anomalous transport with distance in the column (Bromly and Hinz, 2004).

Table 1Estimated values of parameters, determination coefficient r^2 and root mean square error RMSE for CDE and MIM at different distances in the heterogeneous soil column.

Distance (cm)	CDE				MIM				
	ν (cm/min)	D (cm ² /min)	r^2	RMSE	ϕ	D_m (cm ² /min)	$\omega \times 10^5$ (1/min)	r^2	RMSE
100	1.120	3.10	0.986	0.0455	0.579	3.22	2.39×10^{-5}	0.986	0.0458
200	1.129	14.06	0.964	0.0601	0.543	8.23	15.10	0.972	0.0521
300	1.054	13.42	0.969	0.0616	0.560	6.11	18.80	0.989	0.0332
400	1.045	23.28	0.962	0.0629	0.566	9.92	12.44	0.978	0.0467
500	1.153	20.45	0.982	0.0534	0.531	8.04	8.22	0.991	0.0360
600	1.136	71.89	0.978	0.0542	0.526	21.69	8.25	0.997	0.0199
700	0.817	168.50	0.989	0.0346	0.767	142.89	1.85	0.989	0.0338
800	1.083	149.10	0.984	0.0460	0.571	87.58	2.87	0.991	0.0381
900	0.997	95.91	0.988	0.0419	0.624	73.00	1.78	0.990	0.0372
1000	0.902	95.64	0.990	0.0372	0.666	56.85	3.57	0.995	0.0254
1100	0.895	118.20	0.992	0.0301	0.673	77.63	3.09	0.995	0.0243
1200	0.880	93.67	0.988	0.0375	0.690	60.49	2.94	0.990	0.0330
mean	1.018	72.27	0.9792	0.0471	0.608	46.31	7.18	0.9882	0.0355
min ^a	0.817	3.10	0.9595	0.0301	0.526	3.22	1.78	0.9716	0.0199
max ^b	1.153	168.50	0.9915	0.0630	0.767	142.99	18.82	0.9965	0.0521
std ^c	0.117	56.86	0.0117	0.0112	0.076	44.08	5.93	0.0071	0.0096
200–1200 ^d	0.980	79.79	0.9092	0.1030	0.563	19.20	11.10	0.9482	0.0778

^a Min denotes minimum value.^b Max denotes maximum value.^c Std denotes standard deviation.^d 200–1200 means simultaneous fit at all depths except 100 cm.**Table 2**Estimated values of parameters, determination coefficient r^2 and root mean square error RMSE for CLT, FADE and CTRW at different distances in the heterogeneous soil column.

Distance (cm)	CLT				FADE					CTRW						
	μ_l	σ_l	r^2	RMSE	ν (cm/min)	D (cm ^o /min)	φ	r^2	RMSE	ν_ψ (cm/min)	D_ψ (cm ² /min)	β	t_1 (min)	t_2 (min)	r^2	RMSE
100	5.132	0.232	0.9858	0.0456	–	–	–	–	–	8.060	15.76	1.021	1.67×10^{-5}	2.97×10^{-1}	0.9852	0.0467
200	5.063	0.342	0.9625	0.0599	1.150	2.757	1.661	0.9682	0.0625	7.233	13.67	1.011	1.01×10^{-1}	1.47×10^7	0.9848	0.0383
300	5.166	0.285	0.9625	0.0614	1.070	2.999	1.611	0.9767	0.0562	7.150	13.32	1.050	1.84×10^{-2}	1.05×10^6	0.9920	0.0284
400	5.151	0.324	0.9598	0.0628	1.000	7.451	1.798	0.9488	0.0763	7.102	13.09	1.059	1.91×10^{-2}	2.86×10^6	0.9861	0.0371
500	5.089	0.261	0.9797	0.0532	1.160	9.109	1.838	0.9840	0.0513	7.104	12.88	1.077	2.34×10^{-2}	3.48×10^6	0.9935	0.0301
600	4.987	0.437	0.9748	0.0535	1.140	11.01	1.660	0.9855	0.0458	7.088	12.88	1.027	1.77×10^{-1}	2.43×10^6	0.9954	0.0233
700	5.077	0.682	0.9884	0.0347	0.810	26.66	1.696	0.9887	0.0362	7.052	113.24	0.992	3.34×10^{-2}	3.55×10^6	0.9856	0.0396
800	4.943	0.542	0.9837	0.0454	1.050	29.59	1.750	0.9854	0.0430	7.144	51.91	1.013	2.59×10^{-1}	3.53×10^5	0.9897	0.0362
900	5.117	0.438	0.9873	0.0415	1.000	23.04	1.760	0.9891	0.0391	7.012	106.49	1.025	1.03×10^{-1}	1.01×10^4	0.9902	0.0364
1000	5.219	0.437	0.9893	0.0368	0.900	22.98	1.780	0.9919	0.0341	7.057	48.66	1.002	1.51×10^{-1}	2.34×10^5	0.9949	0.0255
1100	5.209	0.459	0.9916	0.0300	0.900	22.43	1.752	0.9929	0.0306	7.082	159.00	1.003	1.22×10^{-1}	5.04×10^4	0.9947	0.0239
1200	5.270	0.403	0.9876	0.0375	0.890	17.06	1.750	0.9885	0.0419	7.069	28.96	1.002	1.29×10^{-1}	3.98×10^4	0.9901	0.0335
Mean	5.119	0.404	0.9794	0.0469	1.006	15.92	1.732	0.9818	0.0470	7.099	52.19	1.024	1.03×10^{-1}	2.62×10^6	0.9906	0.0320
Min ^a	4.943	0.232	0.9598	0.0300	0.810	2.757	1.611	0.9488	0.0306	7.012	12.88	0.992	1.84×10^{-2}	1.01×10^4	0.9848	0.0233
Max ^b	5.270	0.682	0.9916	0.0628	1.160	29.59	1.838	0.9929	0.0763	7.233	159.00	1.077	2.59×10^{-1}	1.47×10^7	0.9954	0.0396
Std ^c	0.095	0.127	0.0116	0.0112	0.120	9.638	0.068	0.0130	0.0136	0.059	51.23	0.027	7.65×10^{-2}	4.26×10^6	0.0039	0.0060
200–1200 ^d	5.091	0.468	0.9319	0.0892	0.981	10.752	1.562	0.9257	0.0936	9.131	17.28	0.990	3.08×10^{-2}	7.33×10^9	0.9612	0.0578

^a Min denotes minimum value.^b Max denotes maximum value.^c Std denotes standard deviation.^d 200–1200 means simultaneous fit at all depths except 100 cm.

For MIM, as shown in Table 1, the values of mobile water fraction ϕ are between 0.50 and 0.60 at distances less than 700 cm except the one at 700 cm (0.767). For distances greater than 700 cm, the ϕ values are all larger than 0.60 except the one at 800 cm (0.571). The remarkable variation of ϕ values around 700 cm is the result of special heterogeneities around this distance. The existence of immobile water in the column was also verified by Huang et al. (1995) as the estimated effective porosity of the column ($=0.23$) was much smaller than the measured total porosity of the column ($=0.37$). With the increase of mobile water fraction, the contact areas between the mobile and immobile regions increase, enhancing solute mixing between these two regions. A higher degree of mixing favors the development of Fickian transport (Padilla et al., 1999). This, in turn, causes the BTCs to become more regular at distances of 800 cm and 1000 cm than those at dis-

tances of 400 cm and 600 cm, as shown in Fig. 1. Based on the fitted ϕ values, the mobile pore-water velocity in the column (v_m) is estimated to be between 0.842–1.228 cm/min.

In Table 1, the dispersion coefficient values of MIM are much lower than those of CDE at same distances, and the rates of increase of the MIM dispersion coefficients are smaller than those of CDE dispersion coefficients. This may be due to that MIM separates solute spreading into dispersion in mobile region and mobile-immobile mass transfer, while the distribution of flow velocity in the mobile region is relatively uniform. With respect to mass transfer coefficient ω of MIM, it has a tendency to decrease with distance as shown in Table 1. This is an indication of the correlation between advection residence time and mass transfer timescale (Maraqa, 2001; Haggerty et al., 2004).

Fig. 2. The breakthrough curves at all distances except the one at 100 cm were simultaneously fitted using each of the five models (CDE, MIM, CLT, FADE and CTRW). Examples of simultaneous fitting results at distances of (A) 400 cm, (B) 600 cm, (C) 800 cm, and (D) 1000 cm are shown, respectively.

The μ_1 values for different distances in CLT are all around five in Table 2. This is expected as μ_1 is primarily dependent on flow velocity in the column. A fundamental assumption of stochastic-convective transport for CLT is that the equivalent dispersivity for CLT increases linearly with travel distance and σ_1 remains constant (Bromly and Hinz, 2004). However, one can see from Table 2 that σ_1 changes significantly over distances. This indicates the unsuitability of CLT for describing solute transport in the column.

Similar to CDE, the fitting velocity values of FADE vary dramatically with distance within the range of 0.810–1.160 cm/min, as shown in Table 2. The velocities estimated by CDE, MIM and FADE are of the same magnitude as measured by Huang et al. (1995). The estimated ϕ values are in the range of 1.611–1.838, which are smaller than 2. This implies that solute transport is anomalous. Both variations in the fitting velocity and ϕ values are due to the heterogeneous nature of soil in the column. From Table 2, it is notable that the dispersion coefficient of FADE also increases with distance, but the rates of increase of the FADE dispersion coefficients is generally smaller than those of CDE dispersion coefficients. This suggests that scale-dependence of dispersion also exists in FADE, but to a less degree than that in CDE. This finding is contradictory to the original idea of using FADE to resolve the scale-dependent dispersion issue.

From Table 2, it is seen that the β values of CTRW at different distances are all close to 1. This implies that highly anomalous transport dominates over the soil column. The v_ψ values are approximately constant (about 7 cm/min) and larger than the

velocity values in CDE, MIM and FADE. This is due to that v_ψ represents the average solute particle velocity and not the average fluid velocity used in CDE, MIM and FADE (Berkowitz and Scher, 2008). The values of cut-off time t_2 for the truncated power-law transition-time distribution function are very large except that at 100 cm, indicating that transition to Fickian transport has not yet occurred. The median transition time t_1 is indeed small with respect to the time span of the BTC. As a result, the transition-time distribution is primarily controlled by β . As the β value remains nearly constant with distance, it seems that the truncated power-law distribution function is able to quantify the full spectrum of anomalous transport behaviors using a single β together with a cut-off and medium time scale. However, the D_ψ values of CTRW change dramatically with distance (see Table 2). At the distances less than 700 cm, the values of D_ψ are around 13 cm²/min. For distances greater than 700 cm, the D_ψ values are larger than those at the distances less than 700 cm, and they vary dramatically with distance. This result is due to that the CTRW theory used here may only account for stationary media. It does not reflect the multiple-scale heterogeneities with a single dispersion coefficient.

Comparison of predicting results of five models

The predictive ability is a critical test of the usefulness of a model. With the parameters obtained by fitting the BTC at 200 cm, pre-

dictions at subsequent distances were made. The measured and predicted BTCs at distances of 400 cm, 600 cm, 800 cm and 1000 cm are shown in Fig. 3. The associated r^2 and RMSE values are listed in Table 3. As expected, the closer the point to the 200 cm, the better of the prediction.

In Fig. 3, CDE and CLT predict different concentrations, while FADE and CDE predict similar concentrations. Compared to CDE and FADE, CLT gives somewhat better predicting results. However, CDE, CLT and FADE are less satisfactory to predict the BTCs, as illustrated in Fig. 3. Compared to CDE, CLT and FADE, the predicting results of MIM are more satisfactory. This is also indicated by the larger r^2 and small RMSE values of MIM than those of CDE, CLT and FADE, as shown in Table 3. However, the MIM cannot simulate the tails of BTCs adequately. As shown in Fig. 3, CTRW captures the evolution of BTCs, especially their tails. This result again demonstrates the applicability of CTRW in characterizing anomalous transport in the column.

Physical interpretation of model performance

From above fitting and predicting results, it appears that CTRW and MIM can better describe the anomalous transport in the large heterogeneous soil column than CDE, CLT, and FADE. The poor performance of CDE for describing solute transport in the column is expected since CDE is designed for Fickian transport, not anomalous transport that seems to be the prevailing process in the column.

The less satisfactory performance of CLT for describing anomalous transport in the column may be primarily due to the assumption of a lognormal travel time probability density function for CLT. This assumption is primarily for mathematical convenience, and its physical relevance is questionable sometimes. In addition, the choice of lognormal travel time pdf requires that soil can be conceptualized as independent stream tubes without lateral mixing of solute, and the solute needs to be applied uniformly over the intake area (Jury, 1982). However, in the experiment of Huang et al. (1995), there should be some degree of lateral mixing between regions of different velocities as a result of highly heterogeneous nature of the soils. Furthermore, flow in some parts of the column becomes three-dimensionally tortuous because of the heterogeneous makeup in the column, especially the existence of clay lenses and mixtures of soils with widely different hydraulic properties (Huang et al., 1995).

The spatial FADE was developed to describe solute particle motion based on spatial Lévy flight. A necessary condition for the Lévy flight is that the medium contains high- and low-permeability streaks, leading to fast and slow flow (Berkowitz et al., 2002). However, the soil column in the experiment discussed above may not have such features. This may explain the less satisfactory performance of FADE for describing anomalous transport in the column.

The MIM divides the heterogeneous medium into two distinct regions with mass exchange. It approximately represents the continuous distribution of flow field with a piecewise distribution: mobile and immobile. Therefore, it can effectively account for the

Fig. 3. Parameters determined at 200 cm were used to predict the breakthrough curves at subsequent distances using each of the five models (CDE, MIM, CLT, FADE and CTRW). Examples of predicting results at distances of (A) 400 cm, (B) 600 cm, (C) 800 cm, and (D) 1000 cm are shown, respectively.

Table 3

Values of determination coefficient r^2 and root mean square error RMSE as the indicators of performance for CDE, MIM, CLT, FADE and CTRW using parameters determined at 200 cm to make predictions at subsequent distances.

Distance (cm)	CDE		MIM		CLT		FADE		CTRW	
	r^2	RMSE	r^2	RMSE	r^2	RMSE	r^2	RMSE	r^2	RMSE
300	0.9201	0.0894	0.9678	0.0567	0.9009	0.0995	0.9157	0.0922	0.9794	0.0445
400	0.9050	0.0955	0.9695	0.0542	0.9085	0.0937	0.8893	0.1041	0.9699	0.0512
500	0.9713	0.0627	0.9526	0.0806	0.9671	0.0671	0.9748	0.0593	0.9449	0.0928
600	0.8992	0.1050	0.9385	0.0820	0.9654	0.0615	0.8992	0.1069	0.9406	0.0705
700	0.4114	0.2443	0.8654	0.1168	0.5903	0.2039	0.4060	0.2484	0.8545	0.1276
800	0.8378	0.1408	0.9183	0.1000	0.9424	0.0839	0.8351	0.1445	0.9315	0.0856
900	0.8346	0.1486	0.9225	0.1018	0.9365	0.0921	0.8296	0.1521	0.9236	0.0974
1000	0.6789	0.2005	0.9538	0.0760	0.8288	0.1464	0.6745	0.2030	0.9535	0.0713
1100	0.5673	0.2140	0.9532	0.0704	0.7645	0.1579	0.5617	0.2164	0.9652	0.0667
1200	0.4345	0.2515	0.9437	0.0794	0.7234	0.1759	0.4292	0.2539	0.9526	0.0625
mean	0.7460	0.1552	0.9385	0.0818	0.8528	0.1182	0.7415	0.1581	0.9416	0.0770
min ^a	0.4114	0.0627	0.8654	0.0542	0.5903	0.0615	0.4060	0.0593	0.8545	0.0445
max ^b	0.9713	0.2515	0.9695	0.1168	0.9671	0.2039	0.9748	0.2539	0.9794	0.1276
std ^c	0.2086	0.0683	0.0307	0.0198	0.1248	0.0491	0.2095	0.0688	0.0351	0.0245

^a Min denotes minimum value.

^b Max denotes maximum value.

^c Std denotes standard deviation.

anomalous BTCs observed in the large heterogeneous soil column. In addition, the relatively high flow rate used in the experiment may generate non-equilibrium conditions at the microscopic or pore scale. This could be one of the reasons that MIM performs better than CDE and CLT. However, as MIM only uses a single-rate of mass transfer, it fails to describe the late tailing exactly observed in above experiment.

The CTRW incorporates the broad spectrum of transition rates or times intrinsic to disordered media (Berkowitz et al., 2006; Berkowitz and Scher, 2008). It allows multiple rates of transport with power law tail waiting times (Bromly and Hinz, 2004). Sequentially, it can better capture the full evolution of plume migration in the soil column, especially the distinct late tailing.

Another reason for different model performance is that these five models have different number of fitting parameters. CDE and CLT have two fitting parameters. MIM and FADE have three fitting parameters, while CTRW have five fitting parameters. Consequently, these five models differ naturally in their flexibility to fit the observations. It is expected that better fits of BTCs are usually obtained from models with more fitting parameters. Therefore, the best performance of CTRW among the five models is probably not only because its concept is appropriate, but also it has the most fitting parameters.

General evaluation of five models

As we know, each model has its own advantages and disadvantages for application. To make the comparison of these five models more general beyond the specific experimental condition discussed above, we present a generic evaluation of these five models in the following.

CDE

The CDE is derived on the presumption that effective parameters can be used and remain constant above a certain scale. However, heterogeneities of porous media present at all scales from sub-millimeter pore scale to basin scale. Therefore, it is often unlikely for CDE to define constant effective parameters to capture the evolution of heterogeneity over a broad range of scales (Berkowitz et al., 2006).

Despite the fundamental drawback of CDE, the mathematical form of CDE is simple with only two parameters (D and ν). There-

fore, CDE can be easily applied to multi-dimensional steady and/or transient flow, saturated–unsaturated porous media, as well as arbitrary initial and boundary conditions. Various chemical reactions can also be incorporated in CDE. Many software packages such as HYDRUS-1/2/3D and MT3DMS were developed based on CDE to interpret tracer transport problems under laboratory and field conditions. Using CDE at local scale, many upscaling methods such as volume averaging and stochastic approaches were proposed to describe solute transport in heterogeneous porous media at large scales (Berkowitz et al., 2006; Frappiat and Holeyman, 2008; Neuman and Tartakovsky, 2008).

CLT

The critical problem of CLT is the assumption of lognormal travel time pdf, which has been discussed above. Second, the CLT travel time pdf and associated parameters are sensitive to the conditions upon which they are applied. Finally, as a result of the black-box nature of the travel time pdf, CLT often cannot yield a great deal of physical insights into the transport process involved.

Compared to CDE, CLT performs better. That is partially because that the effective dispersivity obtained from CLT increases linearly with the travel distance (Zhang et al., 1994; Bromly and Hinz, 2004). This is in contrast with the constant dispersivity used in CDE. Using a linearly increasing dispersivity over scale in CLT enables it to capture the nature of transport in heterogeneous medium to certain extent. Second, CLT is sometimes found to predict solute leaching at deeper depths in some field drain system quite successfully based on shallow depth measurements (Jury and Roth, 1990; Gauer et al., 2006). This may be attributable to the unique nature of the travel time pdf used in CLT (see Eq. (7)). As can be seen from Eq. (7), the travel time pdf at an arbitrary scale x is directly related to that at the reference scale l . Third, to account for partially lateral mixing, Zhang (2000) developed a generalized transfer function model (GTF) based on CLT, which seems to perform better than CDE and CLT. However, the GTF introduced two additional parameters. Finally, to account for two-dimensional flow in the saturated zone of tile-drained fields, Gauer et al. (2006) developed a two-dimensional model combining CLT for vertical transport with an exponential transfer function for lateral transport, and they applied that model to successfully predict the flux concentrations in a tile-drained field.

FADE

As discussed above, the Lévy flight description of FADE may limit its applicability to describe solute transport in geological formations. Second, the exponent of the fractional derivative φ is a key parameter in FADE. Benson et al. (2001) provided a way to determine φ *a priori* by analyzing the statistics of the hydraulic conductivity field. However, this method requires sufficient and site-specific geological measurements to formulate statistical structure. Moreover, very little is known about the relationship between φ and properties of porous media. Finally, complexity of multi-directional fractional derivatives greatly limits the application of FADE in multi-dimensional problems.

However, the spatial FADE is a potentially useful model of dealing with spatially non-local transport since it describes the spread of solute mass over large distances via a convolutional fractional derivative (Zhang et al., 2007a; Zhang and Benson, 2008). The spatial FADE broadens the applicability of CDE by describing the super-diffusive rapid transport including heavy leading plume edges and faster-than-Fickian growth rates (Benson et al., 2000a,b, 2001). Recently, many extended forms of FADE were developed to describe solute transport in non-stationary (Zhang et al., 2007a) or anisotropic (Meerschaert et al., 2001) porous media.

MIM

As a deterministic model, the physical base of MIM is unambiguous and simple. In addition, the mathematical form of MIM is simple enough to be implemented analytically and numerically in a rather straightforward fashion. As MIM is difficult to account for complex and multi-rate mass transfer process, the MRMT was developed to overcome this shortcoming. It can include solute diffusion from immobile zones with varying sizes and shapes, as well as rate-limited sorption.

The main disadvantage of MIM is that it is difficult to determine the model parameters *a priori*. There are a few methods developed to determine the mobile water fraction and mass transfer coefficient in MIM. For example, Brusseau et al. (1994) used the gravimetric mass balance method to measure the mobile water fraction and determined mass transfer coefficient in an aggregated soil in terms of Fick's law. In addition, these two parameters can be determined by experimental methods such as tension disk infiltrometer (Casey et al., 1999), point-source method (Al-Jabri et al., 2002), and time domain reflectometry (TDR) method (Lee et al., 2000). However, determining these two parameters independently is still a non-trivial task as they appear to be somewhat correlated, and the robust physical meaning of them needs further investigation (Griffioen et al., 1998; Maraqa, 2001).

For MRMT, a critical disadvantage is to determine the distribution of mass transfer coefficients unambiguously. Such a distribution is physically related to diffusion in the micro- and meso-pore geometry of porous media, and may be described in a statistical manner (Haggerty and Gorelick, 1995). Haggerty et al. (2000) investigated the late-time behavior of tracer test BTCs with power law, gamma, and lognormal distributed mass transfer rates. Zhang et al. (2007b) have taken into account the hydrofacies at an alluvial system based on the data from the Lawrence Livermore National Laboratory site to determine the mass transfer rate and the mobile water fraction. The tail of numerically simulated BTCs in the region can be predicted quite accurately using the MRMT with above coefficients. Recently, Gouze et al. (2008) used the X-ray micro-tomography (XMT) to characterize the micrometer-scale matrix structure and properties. Based on this, they proposed a method to compute the MRMT memory function, which contains the information of mass transfer. The computed memory function

of samples collected from the field compared well with that deduced directly from the field-scale tracer tests in the same site at Balearic Islands (Gouze et al., 2008). However, as the physical meaning underlying the mass transfer coefficient distribution is not explicitly clear, further theoretical and experimental studies are needed.

CTRW

The CTRW merits attention because of its generality. It is claimed that it encompasses CDE, single-rate and multiple-rate MIM, as well as spatial or temporal FADE (Berkowitz et al., 2006). In addition, CTRW has been generalized to deal with non-stationary media. For example, Cortis et al. (2004) developed a Fokker–Planck equation with a memory term (FPME) to account for solute transport in non-stationary media. The FPME used CTRW to treat unresolved, small-scale heterogeneities probabilistically and treated the large-scale heterogeneity variations deterministically.

Despite the generality of CTRW for describing anomalous solute transport in porous and fracture media, several issues still need further investigations. First, determination of the joint probability density function $\psi(s, t)$ in CTRW requires further research. The choice of $\psi(s, t)$ must be dictated by the physics of flow field. For media such as a “random” fracture network (RFN), $\psi(s, t)$ might be estimated independently from their microgeometry (Berkowitz and Scher, 1997, 1998). Berkowitz et al. (2008) and Berkowitz and Scher (2008) summarized some studies about determining the transition-time probability density function, $\psi(t)$, which is the zero spatial moment of $\psi(s, t)$. However, these studies were limited to porous media with idealized geometries. How to obtain the appropriate choice of $\psi(s, t)$ for different types of geological structures and flow conditions is still a research question. Furthermore, linking $\psi(s, t)$ to particular physical information explicitly is not well known.

Second, a straightforward procedure should be developed to determine the parameters in CTRW. In CTRW, there are several more parameters in $\psi(t)$ in addition to the velocity v_ψ and the generalized dispersion coefficient D_ψ . The spreading parameter β of CTRW can be estimated *a priori* by analyzing the velocity field. Other parameters may have to be determined by curve fitting. However, the uniqueness of the fitted parameters is usually unknown and those fitted parameters may not reflect the actual transport processes. Although some studies try to connect the parameters of CTRW to physical systems (Berkowitz et al., 2008), systematic experimental studies have not yet been conducted to explore the effects of soil physical properties, fluid velocity, transport distance, and water content on specific parameters of CTRW.

Third, the application scope of CTRW can be extended. To our knowledge, most of studies about CTRW were focused on simple initial and boundary conditions. In principle, CTRW is not restricted to infinite or semi-infinite transport domains and different boundary conditions may be incorporated. Further studies are necessary to derive analytical solutions for CTRW under rather general initial and boundary conditions. Although CTRW has been used to study reactive solute transport (Margolin et al., 2003; Cortis et al., 2006; Berkowitz et al., 2008), systematic studies can be conducted to explicitly account for chemical and biogeochemical reactions such as decay, production, and precipitation/dissolution. Furthermore, current CTRW theory is restricted to solute transport in steady-state uniform flow. Further research is needed for complex flow conditions such as transient flow and radial flow. In addition, studies using CTRW to interpret solute transport in multi-dimensional systems were limited.

Summary

In this study, we compared the applicability of the convection–dispersion equation (CDE), the mobile–immobile model (MIM), the convective lognormal transfer function model (CLT), the spatial fractional advection–dispersion equation (FADE), and the continuous time random walk model (CTRW) for describing solute transport across a range of travel distances in a large and highly heterogeneous soil column. The capability of these five models in fitting and predicting BTCs at different distances was thoroughly evaluated. The dependence of the estimated parameters on distances was also investigated.

The measured BTCs demonstrated notably irregular shape and distinct tailing, indicating highly anomalous transport. The fitting and predicting results of CDE, CLT and FADE were found to depart significantly from the measured results, and parameters used in CDE, CLT and FADE were largely dependent on the transport distance. This result indicated the less satisfactory performance of CDE, CLT and FADE for describing anomalous transport in the column. In contrast to CDE, CLT and FADE, the fitting and predicting solute concentrations of MIM were in better agreement with the observed ones. However, MIM was unable to account for the long tailing of BTCs adequately. Compared to MIM, CTRW provided much better description of the long tails of BTCs. In addition, the CTRW spreading parameter (β) was close to 1 and remained approximately constant at different travel distances, implying notably anomalous transport in the column.

To make the comparison of these five models more general, we evaluated the advantages and disadvantages of these five models under generic conditions in terms of their theory framework and *a priori* knowledge of the model behaviors. This generic comparison is useful to provide a good understanding of the differences among the models, and to shed lights on model applications and additional model development.

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