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Continuous time random walk analysis of solute transport in fractured porous media

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[1] The objective of this work is to discuss solute transport phenomena in fractured porous media, where the macroscopic transport of contaminants in the highly permeable inter-connected fractures can be strongly affected by solute exchange with the porous rock matrix. We are interested in a wide range of rock types, with matrix hydraulic conductivities varying from almost impermeable (e.g., granites) to somewhat permeable (e.g., porous sandstones). In the first case, molecular diffusion is the only transport process causing the transfer of contaminants between the fractures and the matrix blocks. In the second case, additional solute transfer occurs as a result of a combination of advective and dispersive transport mechanisms, with considerable impact on the macroscopic transport behavior. We start our study by conducting numerical tracer experiments employing a discrete (microscopic) representation of fractures and matrix. Using the discrete simulations as a surrogate for the "correct" transport behavior, we then evaluate the accuracy of macroscopic (continuum) approaches in comparison with the discrete results. However, instead of using dual-continuum models, which are quite often used to account for this type of heterogeneity, we develop a macroscopic model based on the Continuous Time Random Walk (CTRW) framework, which characterizes the interaction between the fractured and porous rock domains by using a probability distribution function of residence times. A parametric study of how CTRW parameters evolve is presented, describing transport as a function of the hydraulic conductivity ratio between fractured and porous domains.

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1. Introduction

[2] The internal heterogeneity of fractured porous formations is a significant obstacle to the prediction of solute transport processes [*Berkowitz*, 2002]. The macroscopic transport of contaminants in such systems is mainly carried out in high-permeable, interconnected fractures, but most of the capacity for storing a pollutant is provided by the low-permeability porous matrix. Because of the much slower transport in the matrix, steep concentration gradients may occur between the fractures and the porous blocks, giving rise to a local disequilibrium. The terms "macroscopic" and "local" or "microscopic" are used in this paper to define different scales of interest. The macroscopic scale incorporates a large number of individual fractures and matrix blocks, e.g., between a contaminant source and a monitoring well. In contrast, the local (microscopic) scale is on the order of single fractures and single matrix blocks. The local disequilibrium situation with regard to the solute concentrations in fractures and matrix can lead to significant solute transfer at the fracture/matrix interfaces. This local transfer can strongly influence the macroscopic solute transport in a fractured porous formation, and thus needs to be accounted for in numerical models [*Berkowitz*, 2002].

[3] Generally, the numerical simulation of flow and transport processes in fractured porous media can be performed with discrete models or continuum models [e.g., *Berkowitz*, 2002; *Neuman*, 2005]. Discrete models describe the spatial structure of the fracture-matrix system in great detail on a microscopic level, and thus allow for a more accurate simulation than continuum models. However, since discrete models are limited in their applicability to field problems, upscaling methods are commonly employed to develop macroscopic models, simulating the flow and solute transport behavior in sufficiently large computational cells and assigning suitably averaged "effective" properties to them. In fractured porous formations, where the local disequilibrium between fractures and matrix cannot be neglected, researchers have often applied so-called dual-continuum models [*Barenblatt et al.*, 1960]. Here, the heterogeneous formation is separated into two superimposed, interacting media, one representing the fracture system with high conductivity, the other representing the porous rock matrix with high storage capacity. Because both media are treated as different systems, the flow and transport processes are described by two separate sets of equations coupled by transfer terms to account for the exchange of mass at the common boundary.

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[4] Despite the simplification with regard to neglecting microscopic transport processes, numerical modeling of dual-continuum systems is still a complicated process. For example, different types of dual-continuum approaches are needed depending on the hydrologic characteristics of the porous matrix. In the general form of a dual-continuum model, the regional flow and transport processes take place in both domains. In many formations, however, the regional flow and transport processes in the matrix continuum can be neglected because the hydraulic conductivity of the matrix is almost negligible compared to that of the fracture continuum, such as in crystalline rocks or shale [*Bodin et al.*, 2004]. In such cases, the matrix continuum acts as a local storage domain for the regional flow and transport in the fracture continuum. The governing equation for the matrix continuum can then be simplified by eliminating the macroscopic flow and transport terms so that only the local fluid flow or solute exchange with the fracture continuum needs to be considered. In the first general form of a dual-continuum model, we use the term "dual-permeability" (or mobile-mobile) model; the latter case is referred to as a "dual-porosity" (or mobile-immobile) model [*Simunek et al.*, 2003]. Note that in a dual-porosity model, the local fluid flow between fracture and matrix continua may be neglected, e.g., when the flow field is steady state as assumed in this paper (i.e., no local pressure gradient between fractures and matrix) or when the matrix permeability is sufficiently small. Matrix diffusion is then the only relevant solute transfer process at the fracture-matrix interfaces.

[5] A variety of dual-porosity (mobile-immobile) approaches have been described in the literature, most of which with a focus on solute transport in fractured porous media. Respective models have been developed with simple first-order transfer terms [e.g., *Huyakorn et al.*, 1983a; *Birkholzer and Rouve*, 1994] or more complex higher-order approaches, where local-scale detailed descriptions of diffusive transport are employed in the immobile domain [e.g., *Bibby*, 1981; *Huyakorn et al.*, 1983b, 1983c; *Dykhuizen*, 1990; *Zimmerman et al.*, 1990, 1993; *Birkholzer and Rouve*, 1994]. Note that variations of dual-porosity approaches have also been used to study solute-transport problems in heterogeneous porous media bimodal permeability structures [e.g., *Roth and Jury*, 1993; *Haggerty and Gorelick*, 1995; *Feehley et al.*, 2000; *Flach et al.*, 2004].

[6] Macroscopic modeling of solute transport in dual-permeability (mobile-mobile) systems is conceptually more challenging than in dual-porosity (mobile-immobile) systems. First, the macroscopic transport processes need to be solved for in both continua, which requires determination of hydrologic properties separately for the fractured and the porous domain [e.g., *Teutsch*, 1990; *Gerke and van Genuchten*, 1993a]. Furthermore, the solute-transfer term needs to take into account not only diffusive transport, but also the additional effects of advection and dispersion. Figure 1 schematically illustrates the advective mass exchange between fractures and porous matrix, as solutes migrate within matrix pores (driven by a regional gradient) and encounter flow in transverse fractures. *Birkholzer and Rouve* [1994] proposed a dual-permeability approach with a specific solute transfer term for such advective-dispersive mixing processes. In this approach, a first-order exchange term is determined, based on the macroscopic flow in the matrix continuum and the geometric characteristics of the fracture network. For dual-permeability modeling of heterogeneous soils with high- and low-permeability regions, *Ahmadi et al.* [1998], *Cherblanc et al.* [2003], and *Cherblanc et al.* [2007] developed a volume averaging technique that allows definition of first-order transfer terms for diffusive, dispersive, and advective processes.

[7] As is apparent from the above discussion, dual-continuum models of various types are available for simulating solute transport in fractured porous media. However, while dual-porosity models have quite often been applied to field problems, dual-permeability applications have been less frequent. One of the crucial problems encountered when using dual-permeability models is the determination of the large-scale effective properties, which include the macroscopic flow and transport properties of the two domains, as well as the properties determining solute transfer between the two domains. This is not a trivial task. For example, while a priori estimates of solute transfer coefficients have been proposed for idealized subsurface geometries ([e.g., *Dykhuizen*, 1990; *Zimmerman et al.*, 1990, 1993; *Gerke and van Genuchten*, 1993b; *Gwo et al.*, 1998] (for diffusive matrix transport); [*Birkholzer and Rouve*, 1994] (for advective matrix transport)), they are generally derived from calibration to field measurements. Furthermore, the a priori decision about the appropriate model to be used in a specific field situation, dual-porosity or dual-permeability, can be difficult, depending on the time and length scale of interest as well as the domain properties.

[8] In this paper, we evaluate the applicability of the Continuous Time Random Walk (CTRW) theory for modeling solute transport in fractured porous formations, as an alternative to the traditional dual-continuum approach. The CTRW theory has been developed to explain and model anomalous, i.e., non-Fickian, transport in heterogeneous physical systems [*Scher and Lax*, 1973]. Any deviation from perfect homogeneity induces retardation and/or acceleration of the solute, which cannot be represented by models based on the classical hypothesis of homogeneous transport. CTRW is an effective upscaled method that treats unresolved (small-scale) heterogeneities stochastically and resolved (large-scale) heterogeneities deterministically. CTRW has found many useful applications in hydrogeological problems, including transport of tracers in porous media [*Bijeljic and Blunt*, 2006], fracture networks [*Berkowitz and Scher*, 1995; *Noetinger et al.*, 2001a, 2001b; *Landereau et al.*, 2001], sandstones, sand columns, unsaturated soils [*Cortis and Berkowitz*, 2004], karstic systems [*Anwar et al.*, 2008], the hyporheic zone [*Boano et al.*, 2007], transient flow in highly heterogeneous permeable systems [*Cortis and Knudby*, 2006], flow of emulsions in porous media [*Cortis and Ghezzehei*, 2007], heat transfer in porous media [*Emmanuel and Berkowitz*, 2007], and transport of biocolloids [*Cortis et al.*, 2006].

[9] *Dentz and Berkowitz* [2003] demonstrated that the CTRW method is formally equivalent to the linear multirate mass transfer (MRMT) concept [e.g., *Haggerty and Gorelick*, 1995]. The dual-porosity approach is essentially a MRMT model with a specific mass transfer model accounting for heterogeneity in the solute exchange between mobile and immobile regions. Our study aims at demonstrating that the CTRW framework not only can substitute for dual-

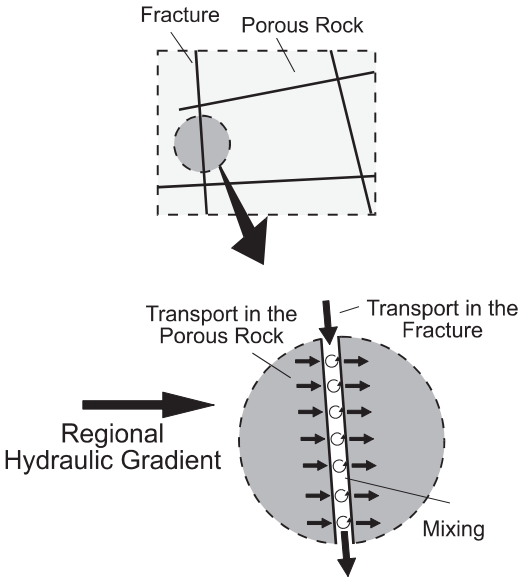

Figure 1. Schematic showing the mixing between fracture and matrix flow as a result of convective transport in the matrix.

continuum approaches, but is generally applicable to fractured porous formations over a wide range of matrix permeabilities. We do this by first conducting numerical tracer experiments in discrete fracture-matrix systems [*Berkowitz et al.*, 1988; *Birkholzer et al.*, 1993a, 1993b; *Birkholzer and Rouve*, 1994; *Rubin et al.*, 1996]. These simulations are assumed to represent the "correct" system behavior. In a second step, the results of the discrete simulations are compared with the results from a nonparametric best fit solution of the CTRW method [*Cortis*, 2007].

2. Discrete Numerical Experiments

2.1. Methodology

[10] Numerical tracer experiments are conducted using a discrete representation of individual fractures and matrix blocks, respectively. Because the flow and transport processes are simulated in great detail on a microscopic ("local") scale, we may assume that the discrete simulation results faithfully represent the transport corresponding to a given set of hydrologic properties, so that the results obtained using the CTRW method can be compared to these "correct" results.

[11] Since our main interest here is phenomena related to fracture/matrix interaction and their impact on macroscopic solute transport, it is reasonable to restrict the discrete simulations to fractured formations with regular geometry and uniform properties. The randomness and heterogeneity of natural fracture networks would (1) create difficulties in interpreting the simulation results with regard to the purpose of our study, and (2) involve the difficult task of assigning effective continuum parameters. Issues of computational efficiency are to be considered as well, since the discrete simulation results need to be compared to continuum results on a sufficiently large scale.

[12] Figure 2 illustrates the setup for the numerical experiments. An idealized formation is considered, with two orthogonal sets of parallel equidistant fractures embedded in porous permeable matrix blocks [*Berkowitz et al.*, 1988; *Birkholzer and Rouve*, 1994; *Lagendijk*, 2005]. A constant (steady state) hydraulic gradient of 0.01 in the positive x-direction is imposed by prescribing appropriate hydraulic head boundary conditions at the inflow and outflow cross sections of the model area. On the local scale, flow in the matrix follows the direction of the gradient, whereas flow in the fractures follows the fracture axis. On the macroscopic scale, however, both types of flow follow the positive x-direction, owing to the symmetry of the fracture network. We simulate the migration of an ideal tracer disposed uniformly along the inflow cross section, given by a relative concentration value of one imposed at the inflow boundary of the model area. The solute migrates through the model area in both the fractures and the porous permeable blocks; however, the transport in the fractures is several orders of magnitude faster. Initially, the model area is not contaminated.

[13] Although the conceptual setup is highly idealized, it is consistent with the requirements needed for the present study. First, it represents the tortuous flow paths through a natural fracture network, providing a large interface for mixing between the fractures and the porous blocks. Second, the flow and transport processes in the domain are symmetrical to the x axis, without any transverse dispersion stemming from the randomness and heterogeneity of the fracture network. It is therefore possible to use the system's symmetry and simulate only the long, thin subdomain depicted in the bottom of Figure 2, with the upper and lower boundaries representing no-flow boundaries. As indicated in the figure, the term "sector" refers to part of the model domain extending between two adjacent fracture intersections. We consider model domains consisting of a hundred, 0.5 m long, sectors, so that the total length of the

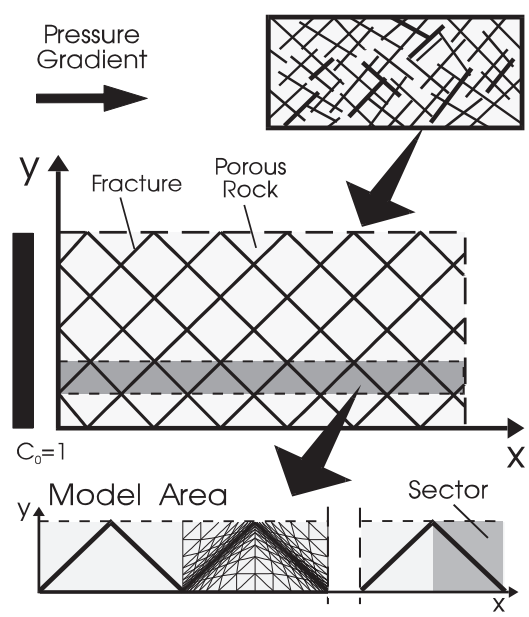

Figure 2. Discrete representation in idealized fracture network. Flow and transport is from left to right, with a concentration boundary condition on the left side. The total domain is 100 sectors long.

Table 1. Geometry and Properties Chosen for Discrete Simulation

Parameter	Value	Unit
Fractures		
Fracture spacing, B	0.707	m
Angle between fractures and x − Direction, θ	45	°
Aperture, a	10^{-4}	m
Hydraulic conductivity of single fracture,[a] K_{si}^F	703	m/d
Continuum conductivity in x − Direction,[b] K^F	9.94×10^{-2}	m/d
Equivalent continuum porosity,[c] n^F	2.83×10^{-4}	-
Longitudinal dispersivity along single fracture, α_l^F	0.01	m
Effective diffusion in single fracture coefficient, D_{mo}^F	10^{-4}	m^2/d
Matrix[d]		
Porosity, n^M	0.05	-
Hydraulic conductivity, K^M	case dependent	m/d
Longitudinal dispersivity, α_l^M	0.01	m
Transverse dispersivity, α_t^M	0.001	m
Effective diffusion coefficient,[e] D_{mo}^M	2.0×10^{-5}	m^2/d
Size of matrix blocks, $B \times B$	0.707×0.707	m^2
Other		
Hydraulic gradient in x − Direction, J	0.01	-
Sector length, L	0.5	m

[a]Calculated from parallel plate assumption as follows: $K_s^F = g(2b)^2/12\nu$.
[b]Calculated from geometry considerations as follows: $K^F = K_s^F \cos\theta/(B \sin\theta)$.
[c]Calculated from geometry considerations as follows: $n^F = a/(B \sin\theta \cos\theta)$.
[d]Properties are given for unit bulk volume of the rock matrix.
[e]Includes effect of tortuosity, assumed to be 0.2.

model domain is 50 m in the x−direction, and 0.5 m in the y−direction.

[14] The discrete simulation runs were performed with the standard GALERKIN-Finite element-Code STRAFE6 using a Crank-Nicholson time weighting scheme [*Lagendijk*, 2005]. Because of the heterogeneity of the formation, a refined discretization in space and time was needed to meet the Peclet and Courant criteria. Triangle elements were used for the porous matrix and one-dimensional line-elements for the fracture representation (see example for two sectors in Figure 2, bottom). A total number of with 1,000 line elements and 20,000 triangles was utilized, and simulation runs comprised up to 30,000 time steps.

[15] Tables 1 and 2 summarize the geometrical and hydrological properties chosen for the discrete simulations. These properties are similar to those used in the discrete numerical experiments described by *Birkholzer and Rouve* [1994] and *Lagendijk* [2005]. The majority of them are kept constant in our study (Table 1), except for the hydraulic conductivity in the matrix, which is varied in four sensitivity cases (Table 2). We expect matrix conductivity to be the most important parameter defining (1) whether the fractured porous formation is a mobile-immobile or a mobile-mobile system, and (2) whether the solute exchange between fractures and matrix is dominated by diffusive or advective processes. All values chosen represent reasonable parameters mentioned in the literature as typical for actual field situations. Notice that the relevant fracture properties in Table 1 are given for single fractures, as represented in the discrete modeling exercise, but have also been converted into fracture continuum parameters, as required in macroscopic continuum approaches (fracture continuum conductivity and fracture continuum porosity).

[16] Table 2 discusses the basic features of the four sensitivity cases. In Case 1, we consider a small hydraulic conductivity in the matrix of 8.3×10^{-6} m/d; i.e., the porous matrix is essentially impermeable. Cases 2 and 3 denote intermediate cases with conductivities of 2.0×10^{-3} m/d and 8.3×10^{-3} m/d, respectively, while Case 4 features a relatively high matrix conductivity of 9.94×10^{-2} m/d. Notice the strong internal heterogeneity reflected in the ratios of fracture to matrix continuum conductivity and transport velocity. With respect to conductivity, these ratios range from 12,000 (Case 1) to 1 (Case 4); i.e., in the latter case, the same magnitude of flow occurs in the two continua. With respect to transport velocity, these ratios range from almost infinite (Case 1) to 250 (Case 4); i.e., in all cases, the transport velocity in single fractures is much higher than the transport velocity in the matrix. As discussed by *Birkholzer and Rouve* [1994], the internal heterogeneity causes a solute-transport behavior in which the fast flow and transport in the fractures is affected by more or less intense solute exchange with the matrix. In the first case, with near-zero matrix permeability, molecular diffusion is the only transport process causing the transfer of solutes between the fractures and the matrix blocks. In the other cases, with increasing matrix conductivity, more and more solute mixing occurs between fractures and the matrix, as a result of advective flow in the matrix, which has a sizable impact on overall transport behavior (see section 2.2).

2.2. Simulation Results

[17] We shall first discuss simulation results on a local scale—i.e., on the scale of single fractures and matrix blocks—to evaluate the basic phenomena of solute transport in fracture-matrix systems. In Figure 3, we present the solute isoconcentration contours for the discrete matrix blocks located in Sectors 3 and 4 of the model area. These sectors are close enough to the contaminant source to feature a fast response, and yet far enough away from it

Table 2. Sensitivity Cases

	Case 1	Case 2	Case 3	Case 4
Formation type	e.g., crystalline rock, shale		e.g., porous sandstone, limestone	
Matrix hydraulic conductivity	8.3×10^{-6} m/d	2×10^{-3} m/d	8.3×10^{-3} m/d	9.94×10^{-2} m/d
Ratio fracture to matrix continuum conductivity	≈12,000	50	12	1
Ratio fracture to matrix transport velocity[a]	$\approx 3 \times 10^6$ m/d	≈12,400	≈3,000	250
Type of fracture-matrix interaction[b]	almost purely diffusive	mostly diffusion	diffusion and advection	mostly advection, strong mixing
Breakthrough characteristics[b]	rapid response, long tail	Between Cases 1 and 4		typical ADE[c] without tailing

[a]Fracture transport velocity is measured along fracture axis.
[b]Based on *Birkholzer and Rouve* [1994].
[c]ADE: Advection-Dispersion Equation.

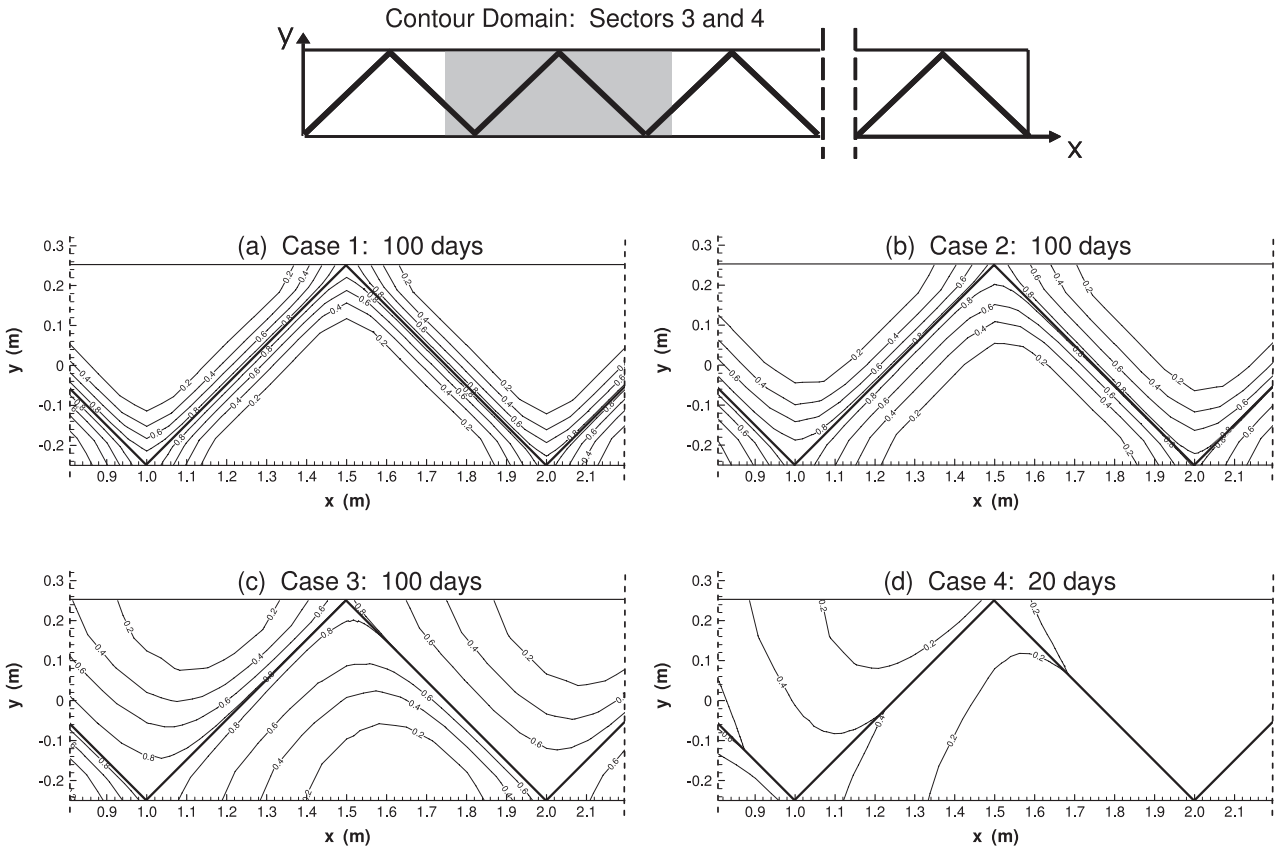

Figure 3. Matrix concentrations from discrete simulations displayed in Sectors 3 and 4 of the model domain.

to be essentially unaffected by the inlet boundary condition. We then discuss the macroscopic transport in the discrete fracture-matrix systems using breakthrough curves (BTC, see Figure 4) obtained at selected locations along the model domain (i.e., at 1 m, 5 m, 15 m, and 45 m from the inflow boundary, which corresponds to 2, 10, 30, and 90 model sectors). The BTCs at these locations will be used to evaluate the performance of the CTRW method.

[18] Figure 3a depicts the discrete simulation results in Sectors 3 and 4 for Case 1, which has an almost impermeable porous matrix. We notice a strong contaminant buildup near the fractures, demonstrating that solutes migrate very fast in the fracture network. During this fast advective transport, a small fraction of the solute migrates from the fractures into the porous matrix. This process is slow: at 100 days, the major fraction of the matrix blocks is not yet contaminated. The BTCs for Case 1 in Figure 4a exhibit the typical transport behavior of dual-porosity (mobile-immobile) media. The tracer breakthrough values initially increase very quickly, because of the large velocities in the fracture network. The smaller the distance between observation point and tracer inlet, the more significant the initial concentration buildup. Long tailing is observed after the initial buildup, a result of the slow diffusive transfer between the fractures and the matrix pore system. The dashed BTC indicates the local concentration differences between fractures and matrix for a migration distance of 30 sectors. It is obvious that the formation would need a very long time to equilibrate: significant local concentration differences can still be observed at 3,000 days.

[19] Concentration contours for Cases 2 and 3 are presented in Figures 3b and 3c, respectively, after 100 days of solute disposal. While the transport velocity in the fractures is still orders of magnitude higher than in the matrix (Table 2), the impact of increasing matrix permeability shows in the microscopic transport behavior. The asymmetrical concentration contours are a result of advective-dispersive transport in the matrix, acting in the positive x-direction. The diffusive transfer from the fractures into the matrix is complemented by this advective-dispersive component; thus, the faster concentration buildup in the matrix compared to Case 1. The effect of enhanced mixing between fractures and matrix also shows in the BTCs in Figures 4b and 4c, where, compared to Case 1, equilibrium conditions are reached earlier and less tailing can be observed.

[20] Case 4 presented in Figures 3d and 4d features a conductivity ratio of one between the fracture and matrix continua; i.e., 50% of the macroscopic flow is performed in the fractures and 50% in the matrix. The advective-dispersive mixing between the fracture and the matrix flow is so intense that the local concentrations equilibrate very fast, despite the still significant velocity-difference ratio of 250 between the two media. We present concentration contours at 20 days because the matrix blocks in Sectors 3 and 4 are completely contaminated after less than 100 days. (With a transport velocity of about 0.02 m/d in the matrix, a particle needs about 50 days to migrate along the two

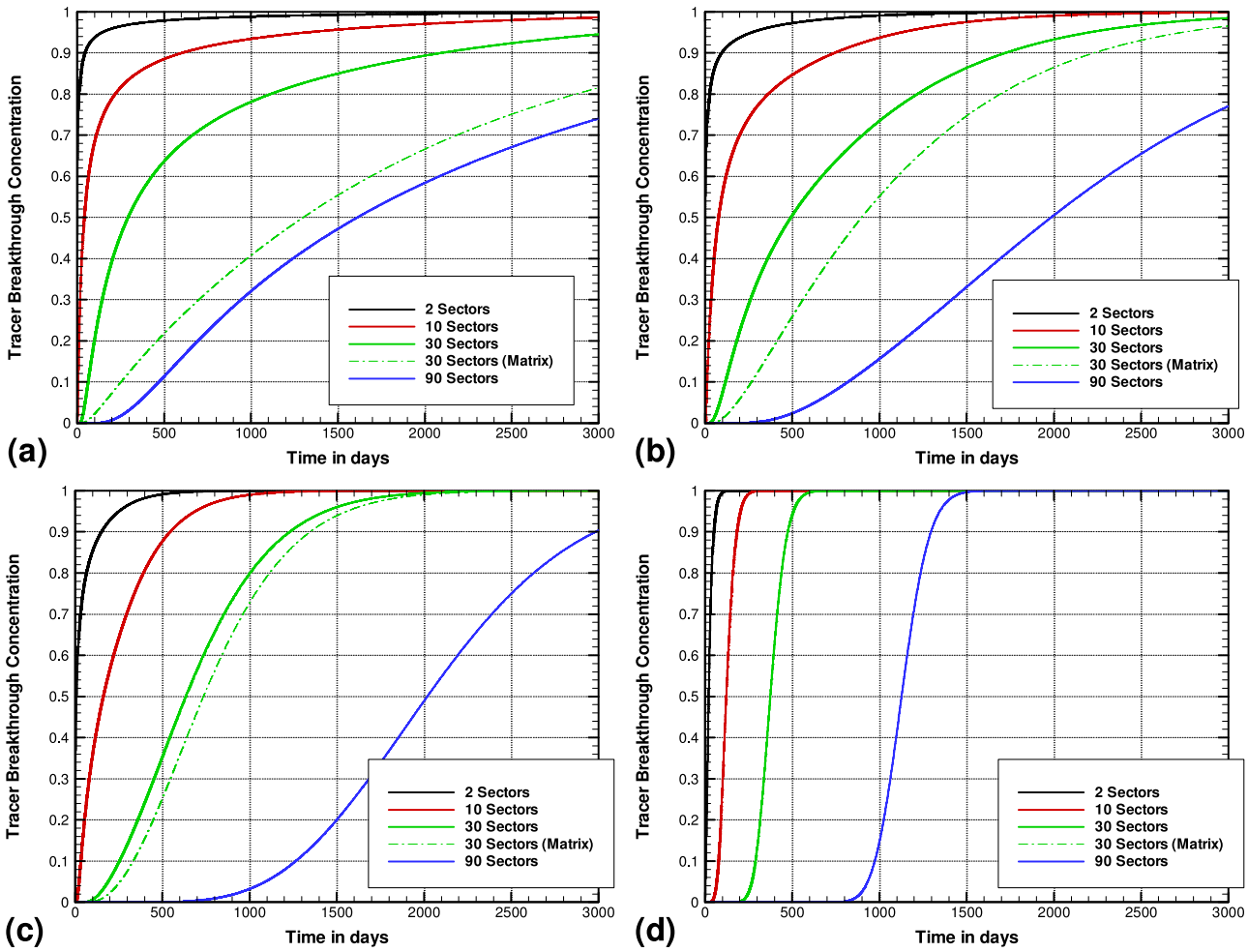

Figure 4. Breakthrough curves for (a) Case 1, (b) Case 2, (c) Case 3, and (d) Case 4, measured at different locations along the model domain.

sectors, as shown in Figure 3d.) The breakthrough curves in Figure 4d resemble those of advective-dispersive transport in a homogeneous medium; it seems that an almost continuous front is moving through the formation.

3. CTRW Modeling of the Fractured-Rock Transport Problem

3.1. Physical Motivation and Model Formulation

[21] The CTRW framework is a generalization of the classical Random Walk (RW) method so often used in the hydrogeological literature to solve the advection-dispersion equation (ADE) of a passive tracer in a porous domain. In the RW approach, tracer density is obtained by following the evolution of an ensemble of random walkers taking (uncorrelated) jumps of constant length at random (uniform) direction in the unit time. CTRW generalizes this physical picture by allowing the walker to jump according to a probabilistic distribution function (pdf), $\Psi(x, \tau)$, of the length of a jump, x, and the retention time, τ, at a given location, while keeping a uniform random distribution for the jump direction. Assuming that the probability of the length of the jumps and the retention time probability are statistically independent, we write $\Psi(x, \tau) = p(x)\psi(\Psi(\tau)$, where p(x) is the probabilistic distribution of the particle jump lengths, and $\psi(\tau)$ is the retention times pdf. A detailed analysis of this uncoupling assumption can be found by *Berkowitz et al.* [2006]. When both the p(x) and $\psi(\tau)$ pdfs have finite first and second moments, (e.g., uniform, decaying exponential), the CTRW and RW physical pictures can be considered to be equivalent. If, however, either of the two has infinite variance (e.g., Cauchy, power law) than the CTRW yields qualitatively different physical pictures, and the random paths are referred to as Levy walks and Levy flights, for the cases of infinite variance of $\psi(\tau)$ and p(x), respectively. By taking an ensemble average over all the possible realizations of the unresolved heterogeneity, it is possible to map the set of small-scale, unresolved heterogeneities onto a probabilistic distribution of retention times, $\psi(\tau)$, that contains all the information necessary to describe transport in a given heterogeneous media. The p(x) pdf is assumed to have finite variance; from a physical point of view, this means that the tracer is allowed to take only relatively short jumps—consistent with the geological picture we have of a fractured porous matrix.

[22] A comprehensive discussion of the CTRW and its relation to other upscaling methods can be found in the recent review by *Berkowitz et al.* [2006]. We refer to this review for the theoretical development of the CTRW, while details regarding the numerical implementation can be

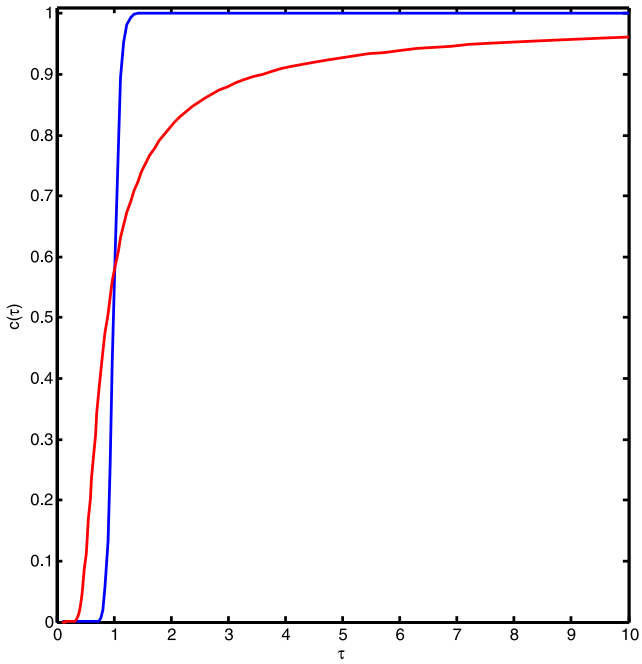

Figure 5. ADE solution (solid line) and CTRW solution (dashed line), for the same value of the non-dimensional dispersivity $\alpha = 0.005$. For the CTRW solution, $\tilde{\psi}(u) = \frac{1}{1+u^{\beta}}$ with $\beta = 0.8$.

found by *Cortis and Berkowitz* [2005]. In this work, we use, as the starting point of our analysis, the CTRW partial differential equation (PDE) for the transport of a passive tracer. In its nondimensional form, the CTRW PDE that governs the spatiotemporal evolution of the density of a passive tracer, c(x,τ), is [*Dentz et al.*, 2004]:

$$u\tilde{c}(x,u) - c_0(x) = -\tilde{M}(u)\partial_x[\tilde{c}(x,u) - \alpha\partial_x\tilde{c}(x,u)] \qquad (1)$$

where the tilde indicates the Laplace transform (LT) $\tilde{f}(u) = L[f(\tau)] = \int_0^{\infty} f(\tau)\exp(-u\tau)d\tau$, u is the Laplace variable, c_0 (x) is the initial condition, α is the local dispersivity, and $\tilde{M}(u)$ is a memory function that takes into account the nature of the heterogeneity and is related to the retention times pdf, $\psi(u)$, by $\tilde{M}(u) = u\frac{\tilde{\psi}(u)}{1-\tilde{\psi}(u)}$. In equation (1), length and times have been made nondimensional, such that the nondimensional transport velocity is equal to unity. Equation (1) represents the time convolution of the memory function M(τ) with the classical advection-dispersion operator, and for this reason this class of models is referred to as nonlocal in time. Equation (1) reduces to the classical ADE when $\tilde{M}(u) = 1$; i.e., M(τ) = $\delta(\tau)$, which implies an exponentially fast decay of the retention times pdf, $\tilde{\psi}(u) = \frac{1}{1+u}$, i.e., $\psi(\tau) = \exp(-\tau)$. It can also be shown that fractional derivative models are special cases of the general CTRW formulation [*Berkowitz et al.*, 2006].

[23] The CTRW interpretation of the dispersivity α is different from the classical advection-dispersion equation (ADE). In the ADE, α represents a typical characteristic length of the small features of the systems, e.g., the pore-throat size. This interpretation has been a problematic one from its inception, and has led to a vast literature on the so-called macroscopic dispersion tensor, i.e., the attempt of explaining the scale-dependent spreading of observed tracer BTCs by means of an evolving characteristic length. Instead, in the CTRW approach, α is defined as the ratio

$$\alpha = \frac{1}{2}\frac{\int p(x)x^2\mathrm{d}x}{\int p(x)x\mathrm{d}x}. \qquad (2)$$

[24] The $\psi(\tau)$ pdf completely describes, in a probabilistic sense, the entire range of interactions that a solute molecule experiences in its interactions with the fluid flow field. Heterogeneities in the flow field have a strong influence on the retention-time probability of staying in a given place for a given interval of time, as is the case for high retention times in stagnation zones (such as those in low-permeability matrix blocks) and short retention times for fast flow paths (such as those in interconnected fractures). In other words, the CTRW approach smoothes out the unresolved heterogeneities and maps them onto the $\psi(\tau)$ retention times pdf. This mapping has the effect of representing the overall effect of the heterogeneities through a time-memory convolution, which reflects the history of interactions within the system.

[25] As discussed by *Dentz et al.* [2004], an algebraically decaying $\psi(t) \sim \tau^{-1-\beta}$ can explain a power law like type of decay for the tail of a breakthrough curve. This type of long tailing is illustrated in Figure 5, where we plotted the solution of the ADE equation for a dimensionless velocity of v = 1 and a dimensionless dispersivity $\alpha = 0.005$ (solid blue line), and the CTRW solution corresponding to the $\tilde{\psi}(u) = \frac{1}{1+u^{\beta}}$, with $\beta = 0.8$, and $\alpha = 0.005$ (solid red line). We recall that the ADE solution corresponds to $\tilde{\psi}(u) = \frac{1}{1+u}$. The long tailing in the CTRW solution is caused by the convolution of the memory function with the ADE transport operator (solid blue line). We note that the explicit solution of the CTRW equation is more than just a simple convolution of the memory function $\tilde{M}(u)$ with the solution for the ADE equation [see, e.g., *Dentz et al.*, 2004, Appendix B]. Depending on the specific shape of $\psi(\tau)$, the CTRW model can reproduce the fast early time arrivals as well as the long tailing typical of fractured systems, as illustrated in Figure 5.

[26] Typically, the CTRW PDE is solved by postulating a simple functional form for $\psi(\tau)$ and then fitting its model parameters to the experimental data. A number of $\psi(\tau)$ models are described in detail by *Berkowitz et al.* [2006]. Despite the wide success in fitting many laboratory and field data sets, however, such simple functional forms may not be general enough to describe the entire range of transport modes encountered in hydrogeological applications [*Anwar et al.*, 2008]. Following this approach, we have tried to fit the BTCs in Figure 4 with all the functional forms described by *Berkowitz et al.* [2006], with no success. Attempts to generalize these functional forms to conform to the shape of these BTCs also failed. Thus a more general and less restrictive method needs to be used in this case. For this reason, in this work we apply a nonparametric inversion algorithm (NPIA) first described by *Cortis* [2007].

[27] The NPIA is aimed at recovering the numerical approximation of the whole spectrum of retention times that govern transport directly from the experimental data, without postulating a priori a functional form for $\psi(\tau)$. While the details of the NPIA can be found by *Cortis* [2007], below we summarize the salient features of the

method. In the NPIA, the $\psi(\tau)$ is given through its numerical representation in the time-interval interest depending on the evolution of the breakthrough. This representation is obtained through the numerical inversion of the numerical approximation of $\tilde{\psi}(u)$, determined via a nonlinear numerical inversion of the best fit of the CTRW PDE solution to the numerical Laplace-transformed data. The method is robust enough to reproduce all the known functional forms for $\psi(\tau)$, and yet flexible enough to represent more complex-looking BTCs. One of the most notable results of the application of the nonparametric approach to nonlocal methods is that any given unresolved heterogeneity can be represented by a family of retention-time probability distributions, $\psi(\tau|\alpha)$ of parameter α, where α is the local dispersivity. In other words, any given set of breakthrough curves taken at different sections, and/or concentration profiles taken at different times, can be fit equally well by different $\psi(\tau)$, conditional to some reasonable value of α. This means that the dispersivity α cannot be considered either an intrinsic or a scale-dependent parameter of the system. Importantly, as no a priori value of α can be given or estimated from any type of macroscopic measurement, it must be interpreted only as an ancillary parameter of the retention-time probability distribution $\psi(\tau)$, which fully describes the transport. These considerations hold true not only for systems exhibiting anomalous transport, but also for normal transport, i.e., for the classical ADE Gaussian type of transport [*Cortis*, 2007].

3.2. Application of the CTRW Method

[28] The first step in applying the CTRW model to the BTCs (shown in Figure 4) is the definition of characteristic (dimensional) transport velocity v' and dispersivity α' for the different fracture-matrix systems studied in section 2.

[29] As discussed earlier, in our CTRW model, the interaction between the fractures and the porous matrix is fully taken into account via the introduction of the memory function $M(\tau)$ (hence the probabilistic distribution of retention times, $\psi(\tau)$, which is convoluted with the classical ADE transport kernel, i.e., $v'\partial_x[c(x, t) - \alpha'\partial_x c(x, t)]$. We thus need to define reasonable values for the relevant parameters v' and α' of the classical ADE that represent the local dispersion inside the porous matrix and along single fractures, without accounting for their interaction.

[30] One logical approach is to define the characteristic transport velocity of the composite system in Figure 2 using the total flux through the fracture-matrix column (to calculate the Darcy velocity) and the total porosity of the fractured porous medium (to convert from Darcy to transport velocity). In other words, we calculate the velocity v' that represents a homogeneous column conducting the same total flux and has the same pore space as the fracture-matrix systems studied in Cases 1 through 4. Note that both these quantities, total flux and porosity, can generally be measured or estimated in field situations. Similarly, the dispersivity α' can be chosen such that it represents only local dispersive effects in fractures and matrix blocks, and not the effects stemming from the fracture-matrix interaction. The exact value of α' is not important because, as discussed above, the application of the nonparametric inversion algorithm implies that equally good fits of the CTRW equations on the BTCs data can be obtained for different (reasonable) values of the dispersivity [*Cortis*, 2007]. In this work, we selected a value of $\alpha' = 0.25$ m, that, as we will see in the discussion below, represent the characteristic dispersivity of Case 4. Such value of α' is considerably smaller than the typical macrodispersivity estimates [*Gelhar*, 1993].

[31] We define dimensionless parameters as follows. Length-based quantities such as horizontal distance or dispersivity are normalized with the total length of the model domain, L = 50 m. The four BTC locations shown in Figure 4, at 2, 10, 30, and 90 sectors (1, 5, 15, 45 m), thus correspond to nondimensional distances of x = [0.02, 0.1, 0.3, 0.9]. Nondimensional dispersivity is $\alpha = 0.005$. The characteristic transport velocity calculated above is normalized to unity, and time in the breakthrough curves is normalized such that a particle migrating with unit velocity would arrive at the end of the column, x = 1, at nondimensional time $\tau = 1$. We then select the BTC calculated at x = 0.1 as the reference BTC for the CTRW model: this will be our "data." In other words, the breakthrough results from the discrete simulations for the cross section at 10 sectors (Figure 4) represent the data set over which the nonparametric inversion algorithm is fitted to. The NPIA yields the $\psi(\tau|\alpha)$ retention time pdf, conditional to the chosen value of α. The $\psi(\tau|\alpha)$ is then used to predict the BTCs at x = 0.02, x = 0.3, and x = 0.9. This procedure is conducted for all parameter cases, by keeping the value of α unchanged.

[32] We recall that Case 1 represents the one bounding case in which a very small flux is allowed to flow in the porous matrix (low permeability). Cases 2, 3, and 4 have increasing matrix-permeability values, with Case 4 the other bounding case, in which an equal amount of flux is allowed in the fractures and the porous matrix.

[33] The results of the fitting procedure to Cases 1 through 4 are reported in Figure 6. In the left panels of Figure 6, we plotted as solid lines the simulated BTCs at the four sections x = [0.02, 0.1, 0.3, 0.9] (as calculated by the discrete numerical procedure), together with the best fits obtained by means of our NPIA applied to the CTRW model (circles). The ADE model $\alpha = 0.005$ is also reported for reference (dashed lines). In the right panel of Figure 6, we plotted, in double logarithmic units as a solid line, the best fit $\psi(\tau)$ obtained with the NPIA on the BTC at x = 0.1 and as a reference the exponential function $\exp(-\tau)$, which represents the ADE model limit.

[34] As we can see from Figure 6, the ADE model does a good job at fitting the BTCs in Case 4 (for x = 0.1) and predicting the BTC at the other sections. This can be seen also from the best fit $\psi(\tau)$ (solid line), which is very close to the decaying exponential $\exp(-\tau)$ (dashed line), i.e., the ADE limit. In other words, the observed "correct" BTC of the fracture-matrix system can be represented without explicitly accounting for unresolved heterogeneities. This is not too surprising, considering the strong mixing between fracture and matrix flow (Figure 3) and the typical symmetrical shape of the breakthrough curve (Figure 4). In this case, however, the CTRW model is slightly more precise than the ADE. Notice that the good agreement between the "correct" BTC and the ADE solution also supports the determination of the characteristic transport velocity of the composite system.

[35] As the total flux in the system predominantly flows in the fractures for the cases with small matrix permeability (Cases 1 through 3), the ADE fails in predicting the BTCs, whereas the CTRW model provides excellent fits (for x =

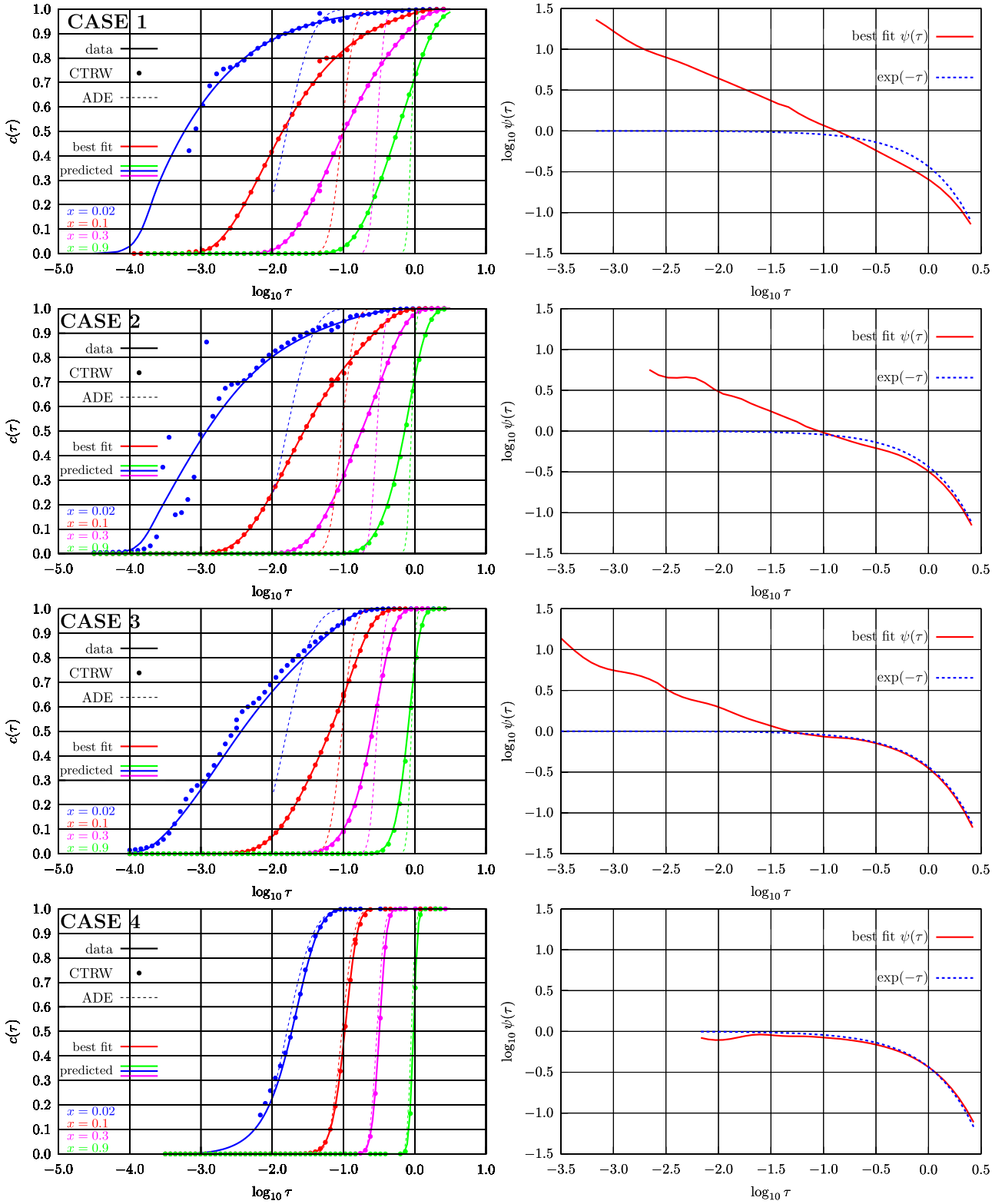

Figure 6. Best fit results of the CTRW model. Cases 1–4, (top to bottom) represent systems with increasing values of the porous matrix (see Table 2). In the left panel we compare the discrete numerical computations (solid lines), with the CTRW model (circles) and the ADE model (dashed lines). The breakthrough curves are calculated at four different sections, x = 0.02, 0.1, 0.3, and 0.9. In the right panel, we plot the best fit probabilistic distribution of retention times, $\psi(\tau)$ (solid lines), and for comparison the decaying exponential $\exp(-\tau)$ (dashed lines), the classical ADE limit.

0.1) and predictions (for x = [0.02, 0.3, 0.9]). (For the section at x = 0.02, the CTRW model provides a correct prediction only up to the time at which the reference BTC used to derive the $\psi(\tau)$ pdf (in our examples the BTC at x = 0.1) differs significantly from zero. In other words, because of the inherent numerical instability of the numerical Laplace inversion algorithms (i.e., the oscillating behavior), the numerical approximation of $\psi(\tau)$ is not accurate enough to back-propagate the BTC for small enough times.) The CTRW approach is capable of representing transport processes for a wide range of fractured porous formations, ranging from mobile-immobile systems with mostly diffusive mixing (Figure 3a for Case 1) to mobile-mobile systems with diffusive as well as advective-dispersive mixing (Figures 3b and 3c for Cases 2 and 3).

[36] In each of these three cases, the best fit $\psi(\tau)$ pdfs consistently deviate from the decaying exponential, which indicates the presence of a wider spectrum of characteristic retention times in the fracture-matrix system. We can observe the graph of the best fit $\psi(\tau)$ (solid line) crossing the graph of the decaying exponential (dashed line). Retention times larger than $\exp(-\tau)$ are indications of faster tracer arrivals, whereas smaller values indicate slower tracer arrivals. This behavior can be understood by recalling the characteristics of the fracture-matrix interaction as shown in Figure 3. We also note that the best fit $\psi(\tau)$ converges, for long times, to a decaying exponential behavior, a clear indication of a truncation time for the transport process [*Dentz et al.*, 2004]. Consistent with this observation, the crossing time decreases with the increase of the matrix permeability.

[37] It is also worth pointing out that the estimated $\psi(\tau)$ pdfs show a $\tau^{-1/2}$ slope for Cases 1 through 3, which is often observed in field conditions and interpreted as macroscopic matrix diffusion. While Cases 1 and 2 are definitely diffusion dominated in the matrix, Case 3 exhibits clearly the effect of advective transport through the matrix blocks. It appears that diffusive and advective interaction between fractures and matrix lead to the same slope in the estimated $\psi(\tau)$ pdfs. This suggests that the macroscopic values of matrix diffusion determined in field conditions, which are often larger than those observed in laboratory conditions, may include contributions stemming from advective transport in the porous matrix. A interesting topic of research would be a study of the relationship between the transition cut-off time from a $\tau^{-1/2}$ slope to a decaying exponential behavior in the $\psi(\tau)$, and its dependence on the permeability characteristics of the fractures and the matrix.

[38] Note that the value for dispersivity α remains unchanged for the four cases, so that the transport is completely defined by the $\psi(\tau|\alpha)$ pdf. Furthermore, within each individual case, a single value of α is used to describe the BTCs for the four locations, whereas a macrodispersivity approach would require a scale-dependent and much larger value of $\alpha = \alpha(x)$. Our sensitivity study indicates that the quality of the CTRW fitting results does not depend on the particular (small) value of α, in accordance with the results of *Cortis* [2007] describing the existence of a family of residence time pdfs parameterized in α. This confirms our initial conjecture that small values of α can be thought of as accounting for the small local dispersion and diffusion phenomena happening in the individual fractures and matrix blocks, whereas the fracture-matrix interaction can be represented by a memory function related to the tracer retention-times probabilistic distribution.

4. Conclusions

[39] We have presented a study of the tracer-transport interaction in a composite hydrogeological system consisting of interconnected fractures and porous permeable matrix blocks. Four sensitivity cases, covering a wide range of matrix permeability values, exhibited a macroscopic transport behavior strongly dependent on the intrinsic heterogeneity of the fractured rock (i.e., fractures versus matrix) and the characteristics of local fracture-matrix interaction processes. Using results from numerical experiments employing a discrete (microscopic) representation of fractures and matrix, we investigated the possibility of the Continuous Time Random Walk (CTRW) framework for predicting the observed macroscopic transport processes in such composite media.

[40] Our results indicate that:

[41] (1) The CTRW offers a valid and robust alternative to classical approaches used for fractured porous media (such as dual-continuum models), with a clear physical interpretation and a parsimonious number of parameters;

[42] (2) The anomalous transport observed in the numerical experiments can be fully characterized by the probabilistic distribution function (pdf) of retention times, $\psi(\tau)$, which stochastically describes the full range of interactions between the fractures and porous matrix;

[43] (3) The $\psi(\tau)$ pdf can be extracted by means of a nonparametric inversion algorithm fitted on the observed breakthrough data at a given location, which fully characterizes the transport at all other locations;

[44] (4) The characteristic transport velocity used in the CTRW approach can be calculated from the total composite flux and the total composite porosity of the fractured formation;

[45] (5) The dispersivity α used in the CTRW is not scale-dependent, such that one value of α can be used for all sensitivity cases and locations. Moreover, the relatively small value used for α represents the local dispersion in single fractures or matrix blocks, but does not need to account for the complex interaction between fractures and matrix that leads to the anomalous macroscopic behavior. As discussed above, the latter is fully characterized by the pdf of retention times;

[46] (6) Anomalous early time arrivals can also be represented in the CTRW framework, and are characterized by values of $\psi(\tau) > \exp(-\tau)$ for times smaller than some crossover value τ', whereas the slow late-time arrivals are characterized by values of $\psi(\tau) < \exp(-\tau)$.

[47] Future work will focus on CTRW applications to more disordered fracture-matrix systems, looking at the effects of random fracture structures or evaluating the impact of microscopic heterogeneities within the fractures or the porous matrix, hence requiring a local $\psi(\tau)$ for these local structures. We will also attempt to apply the CTRW methods developed here to field data from fractured porous media.

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