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A simple and efficient random walk solution of multi-rate mobile/immobile mass transport equations

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ABSTRACT

We extend the particle-tracking method to simulate general multi-rate mass transfer (MRMT) equations. Previous methods for single-rate equations used two-state Markov chains and found that the time a particle spends in the mobile state between waiting time epochs is random and exponentially distributed. Using Bochner's subordination technique for Markov processes, we find that the random mobile times are still exponential for the stochastic process that corresponds to the MRMT equations. The random times in the immobile phase have a distribution that is directly related to the memory function of the MRMT equation. This connection allows us to interpret the MRMT memory function as the rate at which particles of a certain age, measured by residence time in the immobile zone, exit to become mobile once again. Because the exact distributions of mobile and immobile times are known from the MRMT equations, they can be simulated very simply and efficiently using random walks.

1. Introduction

Multi-rate mass transfer (MRMT) equations [11] were developed as an extension of the classical mobile/immobile equations [33] to address a lack of fit to empirical data. The classical single-rate, mobile/immobile model exhibits exponential decay in mobile concentration at late time: once the bulk of the mobile plume has washed away, the remaining immobile contaminants leak out at a rate proportional to their concentration. Since non-exponential breakthrough at late times is often seen, a more flexible model was needed. This was accomplished by adding multi-rates at which tracer moves between mobile and immobile phases [3,11], and eventually by defining a continuum of rates in a "memory function" [4,12]. The resulting MRMT equations can be written as a pair of coupled deterministic partial differential equations in continuous time and space, with one time derivative term replaced by a convolution with the memory function.

Connections between some continuum models of concentration movement and their corresponding descriptions of the dynamics of a single particle have long been known. Einstein [8] showed how a particle undergoing continual discrete random walks tends to approximate a Brownian motion. The probability density of the Brownian motion follows a diffusion-type equation, hence a large number of independent particles will, after sufficient time, closely approximate the concentration profile following the advection–diffusion equation. In the 1940s, Bochner [2] described a stochastic process in which a Markov process (e.g., a Brownian motion) is paused for random periods of time. If the random periods that a particle waits in a motionless state are fairly well behaved (i.e., stationary), then the time that a particle is actively in motion can be calculated. This randomization of active motion time due to pauses is called a subordination of the original active Markovian motion process. In mathematical terms, let $A(t)$ be the position of an uninterrupted Brownian motion at a true elapsed time t. If the time spent actively in motion is another random variable $U(t)$ that also depends on the true or "clock" time t, then the position of the particle is given by $A(U(t))$. We exploit *Bochner's* subordination relationship to derive the exact stochastic process that corresponds to the continuum MRMT equations. The stochastic process naturally invites several simple and efficient numerical implementations using the particle-tracking technique.

Our model is built on a two-state (mobile versus immobile) Markov process. This method was developed in terms of particle-tracking algorithms [32] to extend the analytic solutions for single-rate mass transfer in homogeneous systems embodied in the CXTFIT code [29]. The single-rate particle-tracking model was built to simulate kinetic sorption [32], which was shown to be equivalent to single-rate mass transfer [11]. The single-rate particle-tracking model has been used to approximate microbial filtration and release [19], and mass transfer between fractures and porous blocks [17]. Regarding the latter work, Haggerty and Gorelick [11] showed that diffusion into porous volumes of various shapes

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is more accurately described by a multi-rate model, but a simple mobile/immobile particle-tracking modeling framework that allows a spectrum of rates is still lacking.

The present work can be viewed as an extension of previous single-rate mass exchange models with several new key features. First, any allowable spectrum of rates, defined by the continuum memory function, can be simulated. If either the memory function or the corresponding distribution of the waiting times are known, the stochastic process can be simulated exactly. Second, we relax the previous assumption of a finite mean waiting time in the immobile phase. This describes power-law breakthrough tailing with the same number of parameters as the single-rate model. Third, because we derive the exact probability density function for mobile and immobile times, the effects of an immobile zone can be added to the solution of a mobile-only transport solution, as long as the velocity and dispersion parameters are constant in time and the immobile zone parameters are constant in space. In effect, we add an analytic extension of the CXTFIT methodology to any 3-D boundary value problem with single- or multi-rate mass partitioning.

There is no extra computational expense of our multi-rate particle-tracking model relative to the single-rate models. Other recent methods developed to simulate transport with MRMT include continuous evaluation of mobile moments, which depend on an approximate (and computationally expensive) evaluation of matrix powers [27]. In this method, the probability of changing state is continually calculated, whereas we calculate the time at which the change must occur. Ours is an inherently efficient method that will most often be faster than random walk simulation of the classical advection–dispersion equation, because many particles will be immobile for extended periods of time, significantly simplifying the calculations.

2. Solute transport with multi-rate mass transfer

Mass transfer formulations of transport typically refer to a system of deterministic equations that relate (1) the concentrations in mobile + immobile phases to the divergence of flux in the mobile phase and (2) the transfer of solute mass between a mobile and one or more relatively immobile phases [6,11]. Many models have been built that define the immobile phases as either a solid sorbed phase in contact with mobile water [32], immobile water in pore spaces [6] or a solid sorbed phase in contact with immobile water [29]. Haggerty and Gorelick [11] show that all of these models are equivalent, once the concentrations and total quantity of each phase is properly defined. For example, a sorbed phase concentration is defined by the mass of sorbent per mass of aquifer solids, while solute concentrations is mass of solute per volume of water. If, and only if, the sorbed and dissolved concentrations are constant multiples of each other (linear, instantaneous, and reversible sorption), can the sorbed concentrations in any mobile or immobile phase be represented by the corresponding dissolved concentrations, and all of the aforementioned models can be related to each other [11]. If, on the other hand, the sorbed concentrations do not move lock-step with the surrounding water, then the sorbed and dissolved concentrations must be accounted for separately.

For simplicity here we simply refer to the concentrations in a mobile and a continuum of immobile zones with different fractions of the total porosity. The mobile porosity is denoted θ_M and the sum of all immobile porosities is denoted θ_I. Generalizations to linear and instantaneous (following [11]) or kinetic sorption are straightforward, however in the latter case one must separately keep track of the aquifer solid mass contributing to sorption. Let $C_T(x,t)$ denote the total resident concentration in mass per volume of aquifer material (solid and liquid) at time t at the point x in space, normalized so that $\int C_T(x,t)dx = 1$. Let $C_M(x,t)$ and $C_I(x,t)$ denote the mobile and immobile dissolved concentrations so that $C_T = \theta_M C_M + \theta_I C_I$. Following Schumer et al. [31] we write the MRMT equations of contaminant transport:

$$\begin{aligned}\frac{\partial C_M}{\partial t} + \beta\frac{\partial C_M}{\partial t} \bigstar g(t) &= A_x C_M - C_M(x,t=0)\beta g(t),\\ \frac{\partial C_I}{\partial t} + \beta\frac{\partial C_I}{\partial t} \bigstar g(t) &= A_x C_I + C_M(x,t=0) g(t),\end{aligned} \tag{1}$$

where the capacity coefficient $\beta = \theta_I/\theta_M$, "$\bigstar$" denotes convolution, $g(t)$ is a nonnegative "memory function" that models how long particles stay in the immobile zone, and A_x is a suitable advection–dispersion operator defined below. For classical advection and Fickian dispersion in the mobile phase, we may take $A_x = -\nabla\cdot(v - \boldsymbol{D}\nabla)$. Eqs. (1) assume that all solute begins in the mobile phase: $C_I(x,0) = 0$, although this is easily generalized [4,31]. Multiply the immobile equation by β, add it to the mobile equation, and then multiply the sum by θ_M to get the equation for total concentration $C_T = \theta_M C_M + \theta_I C_I$

$$\frac{\partial C_T}{\partial t} + \beta\frac{\partial C_T}{\partial t} \bigstar g(t) = A_x C_T. \tag{2}$$

In order to connect the MRMT model with the subordinated Markov process model, it is useful to consider the Fourier–Laplace transform of the MRMT equations. Herein, Fourier transform (FT) pairs are denoted $f(x) \Longleftrightarrow f(k)$ and Laplace transform (LT) pairs are denoted $f(t) \Longleftrightarrow f(s)$. Recalling that the Fourier transform of the derivative $(d/dx)f(x)$ is $(ik)f(k)$, the Laplace transform of the derivative $(d/dt)p(t)$ is $sp(s) - p(t=0)$, the Fourier transform of the term $A_x f(x)$ is $A(k)f(k)$, and the transform of a convolution is a product of the transforms, the Fourier–Laplace transform (FLT) of (2) leads directly to

$$C_T(k,s) = \frac{1+\beta g(s)}{s + s\beta g(s) - A(k)}. \tag{3}$$

Here we assume that at time $t = 0$ the total mass $C_T(x, t=0) = \delta(x)$ is concentrated at the origin $x = 0$, so that $C_T(k, t=0) = 1$. Similar calculations, assuming that all particles begin in the mobile phase at time $t = 0$, so that $C_M(t=0) = \delta(x)/\theta_M$, show that $C_T(k,s) = \theta_M C_M(k,s) + \theta_I C_I(k,s)$, where

$$\begin{aligned}\theta_M C_M(k,s) &= \frac{1}{s + s\beta g(s) - A(k)} \quad \text{and}\\ \theta_I C_I(k,s) &= \frac{\beta g(s)}{s + s\beta g(s) - A(k)}.\end{aligned} \tag{4}$$

This gives a simple decomposition into mobile and immobile parts, in terms of the FLT. Since the total mass represented by C_T is conserved, it is clear that the mobile mass is always less than or equal to the total injected mass. The decay rate of mobile mass (assuming all mass initially mobile) is the inverse LT of $1/(s + s\beta g(s))$.

3. The stochastic mobile/immobile model

The model we envision is a particle that travels a random path while mobile, with intervening visits to a immobile state. This state can include sorption or diffusion into an essentially zero-velocity region. Define each epoch in the mobile state by the random variable M and the intervening waiting times in the immobile state by W. The density function of the waiting times is denoted by $\psi_W(t)$.

Bochner's formula [2,9] requires that the motion process $A(t)$ is Markovian. Denote by $a(x,t)$ the probability density of the whereabouts of $A(t)$, and it is well known that $a(x,t)$ follows the Fokker–Planck (Cauchy) equation:

$$\frac{\partial}{\partial t}a(x,t) = A_x a(x,t), \tag{5}$$

where A_x is an advection–dispersion operator, also called a generator. For classical advection and dispersion, take $A(t)$ to be a Brownian motion with drift, and then the generator is $A_x = -\nabla\cdot(v - \boldsymbol{D}\nabla)$. The dispersion operator may be of fractional order for more general Lévy processes [9,20,30]. The Fourier transform solution of (5) for a particle starting at the origin is $a(k,t) = e^{tA(k)}$.

3.1. The operational time process

Several methods may be used to define the time spent in the mobile phase between immobile periods. The process $U(t)$ is also called the "operational time," since it accounts for the random amount of time that a particle "operates" or participates in the motion process. The density of $U(t)$ is denoted by $h(u,t)$ and measures the amount of random time U associated with any deterministic clock time t. See [21,22] for more details.

In general, much more is know about the time spent in the immobile phase than time in the mobile phase. For example, the residence time distributions for particles diffusing into differently-sized low-permeability objects can be calculated [11]. Furthermore, the memory function $g(t)$ in (1) can be approximated based on the thickness distribution of fine-grained sediments [37]. Therefore, we use a duality relationship between the waiting times and the resulting time in motion. The average duration of the mobile periods must be defined relative to the time spent in the immobile zones, since this ultimately defines the "capacity coefficient," and hence the relative mass in mobile versus immobile zones.

Define the capacity coefficient β by the ratio of expected time in the immobile versus mobile zones. For simplicity here we assume a finite mean waiting time—this is relaxed in the Appendix. If the expected time in each immobile period is finite and equal to $E[W] = 1/\lambda$, then the expected time in the mobile phase between each immobilization is $E[M] = 1/\beta\lambda$. Because a mobile particle follows a memoryless Markov process, the time in the mobile phase is exponential. Now $E[W]/E[M] = \beta$, and since the exponential rate parameter is the inverse of the mean, we have $P(M > t) = e^{-\beta\lambda t}$. The process which records the state of a particle (mobile or immobile) is called an alternating two-state Markov renewal process (e.g., [5]). The general ergodic theory of such processes shows that the steady-state mobile probability is p_M, and the steady-state immobile probability is p_I, where

$$p_M = \frac{EM_i}{EM_i + EW_i} = \frac{1/\beta\lambda}{1/\beta\lambda + 1/\lambda} = \frac{1}{1+\beta} \quad \text{and}$$
$$p_I = \frac{EW_i}{EM_i + EW_i} = \frac{1/\lambda}{1/\beta\lambda + 1/\lambda} = \frac{\beta}{1+\beta}.$$

Now we must calculate the relationship between the "clock time" t since a particle leaves the origin $x = 0$ at $t = 0$, and the operational time $U(t)$ that a particle spends in motion. A simple way to do this is to first consider the random clock time $T(u)$ which has passed in terms of a deterministic operational time u. Once we understand the model for $T(u)$, we can easily compute the statistics of its inverse process $U(t)$. Fig. 1 illustrates the link between U and T. Suppose that a particle begins in the mobile phase. Each mobile time M_i is followed by a time W_i in the immobile phase. Let $N(u)$ count the number of exits from the mobile phase experienced by operational time u, i.e., the number of immobilizations. Then the total clock time $T(u)$ which corresponds to u units of time in the mobile phase is the random sum

$$T(u) = u + W_1 + \cdots + W_{N(u)}.$$

The Poisson process $N(u)$ has distribution

$$P(N(u) = n) = \exp(-u\beta\lambda)(u\lambda\beta)^n/n!$$

The relationship between the clock time and mobile time simply sums the conditional probability over any number of jumps

$$P(T(u) \leqslant t) = \sum_{n=0}^{\infty} P(T(u) \leqslant t | N(u) = n) P(N(u) = n).$$

Differentiating each term with respect to t to get the density function, then taking the Laplace transform $t \to s$ and inserting the conditioning probabilities from the Poisson process, we have the density of $T(u)$, denoted $l(s,u)$, of the clock time for any given mobile time u:

$$l(s,u) = e^{-su}\sum_{n=0}^{\infty}[\psi_W(s)]^n \frac{e^{-u\beta\lambda}(u\beta\lambda)^n}{n!} = e^{-su}e^{-u\beta\lambda}e^{u\beta\lambda\psi_W(s)}$$
$$= e^{-su}e^{-u\beta\lambda(1-\psi_W(s))}. \tag{6}$$

Note that the formula for $l(s,u)$ is simply the standard formula for the Laplace transform of a compound Poisson random variable, shifted by u, because the immobile time $W_1 + \cdots + W_{N(u)}$ is a compound Poisson random variable.

3.2. The waiting time process and differential time operators as generators

Because $T(u)$ is an infinitely divisible process whose density $l(t,u)$ has LT $e^{-uL(s)}$, a general theory [22] shows that the process

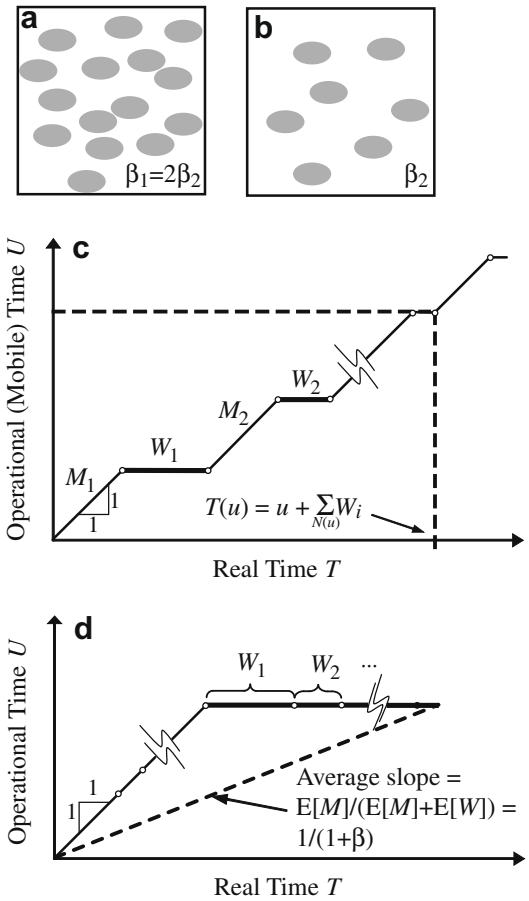

Fig. 1. (a,b) Unit cells representing mobile and immobile (grey) phases. Doubling the number of immobile regions halves the expected time in the mobile phase between sticking events. (c) Accounting for the mobile as well as the immobile phase induces a drift (with slope 1) relating the operational (mobile) time and real (clock) time. For every second of operational time, the clock has ticked one second plus any random time in the immobile phase. (d) A re-ordering of the events (place all time in motion up front and all waits at the end) shows that the clock time is greater than the operational time by a number of random waits. For finite mean waiting and mobile times, the average ratio of mobile to total clock time is $1/(1+\beta)$.

$u = U(t)$, which is the smallest $u > 0$ such that $T(u) > t$, is exactly the inverse to $T(u)$: $T(u) \geqslant t$ is identical to $U(t) \leqslant u$. To make an analogy in discrete terms, the event {number of jumps by time $t \geqslant n$} is the same as the event {time of the nth jump $\leqslant t$}. For example, if at least three jumps have occurred by a time of 1 min, then the time of the third jump had to have occurred before, or exactly at, 1 min, and vice versa (Fig. 1c). The density of the inverse process $U(t)$ can be computed using the density of $T(u)$, because

$$P(U(t) \leqslant u) = P(T(u) \geqslant t) = 1 - \int_0^t l(\tau, u)d\tau,$$

so that the density $h(u,t)$ of $U(t)$ is given by

$$h(u,t) = \frac{d}{du}P(U(t) \leqslant u) = -\frac{d}{du}\int_0^t l(\tau,u)d\tau$$

with Laplace transforms

$$h(u,s) = -\frac{1}{s}\frac{d}{du}l(s,u) = -\frac{d}{du}\frac{1}{s}e^{-uL(s)} = \frac{1}{s}L(s)e^{-uL(s)}. \tag{7}$$

Clearly $(d/du)h(u,s) = -L(s)h(u,s)$ with initial condition $h(u=0,s) = L(s)/s$. Letting $L_t h(u,t)$ be the inverse LT of $L(s)h(u,s)$, and inverting the LT, leads to the governing equation

$$\frac{\partial}{\partial u}h(u,t) = -L_t h(u,t); \quad h(u=0,t) = h_0(t), \tag{8}$$

where $h_0(t)$ has LT $L(s)/s$.

Now, because $T(u)$ is an infinitely divisible process [9] whose density has LT $l(s,u) = e^{-uL(s)}$ with $L(s) = s + \beta\lambda(1 - \psi_W(s))$, as considered in Section 3.1, the formula (7) shows that the inverse process $U(t)$ has a density $h(u,t)$ with LT

$$h(u,s) = (1 + \beta\lambda(1 - \psi_W(s))/s)e^{-us - u\beta\lambda(1-\psi_W(s))}.$$

3.3. The subordinated process

A particle that may spend time in an immobile state will travel a path $A(U(t))$, since it only travels while mobile. Hence the non-Markovian subordinated process $A(U(t))$ describes the motion of a tracer particle that transitions from mobile to immobile phases, and its density $q(x,t)$ solves a space–time governing equation that we may now develop. We call $A(U(t))$ the stochastic mobile/immobile (SMIM) process. The density $q(x,t)$ of $A(U(t))$ can be found by a simple conditioning argument

$$q(x,t) = \int_0^\infty a(x,u)h(u,t)du. \tag{9}$$

The first term $a(x,u)$ models particle motion in linear time and the second term $h(u,t)$ adjusts for the time a particle is *actively* in motion. Taking LT and FT in (9) we get

$$q(k,s) = \int_0^\infty e^{uA(k)}\frac{1}{s}L(s)e^{-uL(s)}du = \frac{\frac{1}{s}L(s)}{L(s) - A(k)} \tag{10}$$

and then we can invert the LT and FT to get the governing equation

$$(L_t - A_x)q(x,t) = \delta(x)h_0(t). \tag{11}$$

The FLT $q(k,s)$ of the SMIM process density is given by (10), with $L(s) = s + \beta\lambda(1 - \psi_W(s))$. It is now possible to equate the SMIM probability density $q(x,t)$ with solutions of the deterministic MRMT equation (2) for total flow. Indeed, the FLT (3) of the deterministic MRMT total concentration, $C_T(k,s)$, is exactly the same as the FLT (10) of the SMIM process density, $q(k,s)$, if we equate $L(s) = s + \beta\lambda(1 - \psi_W(s)) = s + s\beta g(s)$. Hence the uniqueness principle for FLT implies that $C_T(x,t) = q(x,t)$ if we use the memory function $g(t)$ with Laplace transform $g(s) = \lambda(1 - \psi_W(s))/s$. This shows that the MRMT total concentration is the probability density of the SMIM model if and only if

$$g(t) = \lambda P(W > t). \tag{12}$$

This shows that the memory function $g(t)$ is just the probability of waiting in the immobile zone longer than t time units, multiplied by the rate λ at which particles exit the immobile phase. Another view is that the memory function $g(t)$ is the probability of waiting time greater than t normalized by the mean waiting time $1/\lambda$. As noted by Haggerty and Gorelick [11], in the special case that the waiting times are exponential, the probability density of the time in each immobile zone is equal to the memory function: $\psi_W(t) = g(t) = \lambda e^{-\lambda t}$. This will not generally be true. We also note that $g(t)$ must be a probability density, since $\int_0^\infty P(W > t)dt = E(W) = 1/\lambda$, and because $P(W > t)$ decreases monotonically, so must $g(t)$. This gives a concrete interpretation of the MRMT memory function in terms of particle motion. We also note that, using the deterministic MRMT decomposition (4) along with the FLT equivalence, the FLT equations

$$\begin{aligned} q_M(k,s) &= \frac{1}{s + \beta\lambda(1 - \psi_W(s)) - A(k)}, \\ q_I(k,s) &= \frac{1}{s}\cdot\frac{\beta\lambda(1 - \psi_W(s))}{s + \beta\lambda(1 - \psi_W(s)) - A(k)} \end{aligned} \tag{13}$$

partition the SMIM process particle concentration into mobile and immobile phases because $q_M + q_I = q$ in (10). Hence $q_M(x,t) = \theta_M C_M(x,t)$ is the mobile concentration, and $q_I(x,t) = \theta_I C_I(x,t)$ is the immobile concentration. It is important to note that q_M and q_I are the portions of the total probabilities for a particle to occur at some point, hence these are related to the concentration in total (solid and liquid) aquifer material and must be adjusted by porosities to be equated to C_M and C_I. In the Appendix we show how to extend (12) to a fractal memory function that corresponds to an infinite mean random waiting time W. Finally, if one is only interested in the solution of the mobile equation, using the identity $1/b = \int e^{-ub}du$, the first line of (13) becomes

$$\begin{aligned} q_M(k,s) &= \int e^{-uA(k)}e^{-us - u\beta\lambda(1-\psi_W(s))}du \\ &= \int e^{-uA(k)}l(s,u)du, \\ q_M(x,t) &= \int a(x,u)l(t,u)du. \end{aligned} \tag{14}$$

4. Remarks on simulation

Because we have identified the exact non-Markovian SMIM process whose densities solve the MRMT equations, one can obtain numerical solutions to the MRMT equations via particle tracking. Particle-tracking methods are computationally superior to the other standard numerical methods for large flow systems [14,34]. Particle tracking is also the only known method that can simulate multiscaling anomalous dispersion [36], in which multidimensional plume scaling rates are different in each coordinate. Markovian random walk schemes have been developed recently [35] to solve the space fractional advection–dispersion equations, where the solute experiences nonlocal dispersion in space. For mobile/immobile flow, where particles are also delayed in time, a non-Markovian random walk is needed to simulate transport [38]. Recent research [13,26] has given detailed elucidations, objective reviews, and extensive evaluations of random walk methods. A walker (particle) moves in the mobile phase and waits in the immobile phase based on given jump and waiting time densities. This mimics the solute transport through various velocity zones encountered in typical heterogeneous material. By appropriately

assigning the jump size and waiting time for each particle during each jump, the resulting particle number densities approximate $q(x,t)$, $q_M(x,t)$, and $q_I(x,t)$, hence the transport equations (1) and (2).

There are several particle-tracking methods that can be used to simulate mobile/immobile transport. In general, these fall into space- or time-domain techniques. The latter one chooses a specified distance of travel and calculates the random time required to make the journey given some mean advection, random dispersion, and immobilization [7,25]. This method is extremely well-suited to generating breakthrough curves at a fixed arrival plane, but does not provide information about the spatial distribution of concentration (snapshots), or the relative masses in mobile versus immobile phases. The velocity is either assumed relatively constant between specified distances, or is represented by a random variable. Painter et al. [25] give a detailed discussion of implementation and possible future extensions.

The other broad class of particle tracking uses user-defined transport times and moves particles random distances according to the local advection and dispersion values. This space-domain method has been well studied in the case of transport with or without single-rate mass transfer [14,15,23,28,32]. Two subsets of the space-domain method are most useful for multi-rate mass transfer: the small time-step and the time sample path methods. The small time-step method is best when (1) the user wishes to know the whereabouts of particles at a great number of times, for example, to construct a breakthrough curve, or (2) when the mobile transport parameters vary greatly along sample paths so that the advective and dispersive random displacements are already being calculated very often [15,16]. The time sample path method does not impose a minimum time-step and is most efficient when output is desired at a few fixed clock times; however, the immobilization properties (β and $g(t)$) must remain constant over the path of a particle.

The small time-step method simply chooses a random mobile time for each particle. A small, constant time-step is chosen that is much smaller than both the mean mobile and immobile times. Each particle is moved until its mobile time is exceeded by the elapsed time, at which point the particle is assigned (added to the elapsed time) a random immobile time according to the desired distribution. Specifically, the mobile times are exponential with mean $1/\beta\lambda$, where $1/\lambda$ is the mean waiting time (or scale factor for infinite mean, see the Appendix), and the distribution of waiting times follows either (12) or (A.3). When the elapsed time exceeds the immobile time for a particle, it is assigned a new exponential mobile time and begin moving. The whereabouts and phase of all particles can be output at any time-step.

Depending on the value of $1/\beta\lambda$, the time-steps may be very small. Hence we also suggest an indirect approach that decouples the time and motion processes, using the fact that the non-Markovian operational time process $U(t)$ is the inverse of a Markov process $T(u)$. Essentially one first simulates, for each particle, the total amount of operational time U that will occur for a real time t, then moves each particle according to the mobile-only equation as if U was the real time for that particle. To obtain each particle's value of mobile time U, simulate the waiting time process $T(u) = M_1 + W_1 + M_2 + W_2 + \cdots + M_n + W_n$ until the desired clock time t is reached noting whether the final term is M_n or W_n. The amount of mobile time is $U = \sum M_n$, and the final phase of the particle is mobile if the final term is M_n and immobile if the final term is W_n (Fig. 1c). Then simulate each particle's advection–dispersion process $A(U)$. This method assumes that the retention properties that determine each M and W are homogeneous. A similar method for particle tracking, based on operational time, was recently implemented [18].

5. Examples

Next we discuss some specific examples, to illustrate how the general SMIM model relates to many previous conceptualizations of solute transport with partitioning to an immobile phase. In each case, the small time-step method outlined above was used to determine the phase of each particle. To emphasize the effects of mass transfer, we choose a 1-d domain with constant velocity and hydrodynamic dispersion. The advective and dispersive motion of the particles was simulated using standard methods (e.g., [15]).

5.1. Linear retardation

For the simplest case, suppose that each mobile time M_i is accompanied by a constant multiple β of this time in the immobile state, and also suppose that the particle motion process $A(t)$ is a Brownian motion with drift, so that $A(t)$ is normal with mean vt and variance $2Dt$. The particle motion generator in 1-d is then $A_x = -v\partial/\partial x + D\partial^2/\partial x^2$. The density of $T(u)$ is calculated by counting the time in each phase: each motion plus wait accumulates clock time of $u + \beta u$ for every mobile time u. Therefore, $T(u) = u + \beta u$, and the clock time continuously evolves with the operational time. The density of $T(u)$ is $l(t,u) = \delta(t - (1+\beta)u)$. The inverse or operational time process is $U(t) = t/(1+\beta)$ with density $h(u,t) = \delta\left(u - \frac{t}{1+\beta}\right)$ with LT $h(u,s) = (1+\beta)e^{-su-s\beta u}$. By (7), the evolution operator of the surrogate time is $L_t = (1+\beta)\partial/\partial t; h_0(t) = (1+\beta)\delta(t)$. The quantity $1+\beta$ is commonly called the retardation R, and the transport equation for the total concentration (11) is given in more easily identified units: $(R\partial/\partial t + v\partial/\partial x - D\partial^2/\partial x^2)q(x,t) = R\delta(x)\delta(t)$. Thus the retardation factor can be defined in terms of *time* fraction spent in mobile phase in exactly the same way that it is traditionally defined as the *mass* fraction in the mobile phase [1]: $R = \frac{u+u\beta}{u} = \frac{\theta+\rho K_d}{\theta} = 1 + \rho K_d/\theta$. The solution of the transport equation for mobile solute (14) is

$$\theta_M C_M(x,t) = q_M(x,t) = \int_0^\infty a(x,u)l(t,u)du = \int_0^\infty \frac{1}{\sqrt{4\pi Du}} e^{\frac{-(x-vu)^2}{4Du}} \delta(t-Ru)du = \frac{1/R}{\sqrt{4\pi Dt/R}} e^{\frac{-(x-vt/R)^2}{4Dt/R}},$$

in agreement with standard methods [1]. While a particle-tracking technique with mobile periods separated by immobile periods is clearly not the most efficient way to solve this equation, we show the match of the particle tracking to analytic solutions in Fig. 2a. Linear retardation adds one parameter to the classical ADE.

5.2. Exponential immobile times and single-rate mass transfer

Assume immobile waiting times are exponentially distributed $\psi_W(t) = \lambda e^{-\lambda t}$ and that transport in the mobile phase is classical advection/dispersion with generator A_x. The LT of the waiting times is $\psi_W(s) = \lambda/(\lambda + s)$, so the waiting time process $T(u)$ has a density with Laplace transform $l(s,u) = e^{-uL(s)}$ with $L(s) = s + \beta\lambda s/(s+\lambda)$ and temporal generator $\partial/\partial t + \beta\partial/\partial t \star \lambda e^{-\lambda t}$. Therefore, the differential equation for the density of the mobile SMIM process is

$$(\partial/\partial t + \beta\partial/\partial t \star \lambda e^{-\lambda t} - A_x)q_M = \delta(x)\lambda e^{-\lambda t}.$$

Because $\theta_M C_M = q_M$, the mobile phase equation for the MRMT when $C_T = \delta(x)$ is, in agreement with standard methods [11]

$$\frac{\partial C_M}{\partial t} + \beta\frac{\partial C_M}{\partial t} \star \lambda e^{-\lambda t} = A_x(C_M) + \frac{\delta(x)}{\theta}\lambda e^{-\lambda t}.$$

The memory function is $g(t) = \lambda e^{-\lambda t}$, and the jump intensity (Appendix) is $\phi(t) = \lambda \cdot \lambda e^{-\lambda t}$. Now

$$l(s,u) = e^{-su}e^{-u\beta\lambda\left(1-\frac{\lambda}{\lambda+s}\right)} = e^{-su}e^{-u\beta\lambda\left(\frac{s}{\lambda+s}\right)}. \quad (15)$$

We note that the inverse of $\hat{f}(s) = e^{1/s}$ is given by $f(t) = \delta(t) + I_1(2\sqrt{t})/\sqrt{t}$, where I_1 is the first-order modified Bessel function of the first kind. It follows that the real-space representation of (15) is, for $0 < u < t$,

$$l(u,t) = e^{-\beta\lambda u-\lambda(t-u)}\left(\delta(t-u) + \sqrt{\frac{u\beta\lambda^2}{t-u}}I_1\left(2\sqrt{u\beta\lambda^2(t-u)}\right)\right), \quad (16)$$

which can be used in (14) to calculate the effects of single-rate mass transfer (exponential waiting times) on any appropriate time-homogeneous solution to a mobile-only $a(x,t)$. This equation was used as an analytic solution to compare our particle-tracking model (Fig. 2b). The immobile concentration is given by a convolution of the mobile solution (4). See also [29]. The multidimensional $a(x,t)$ in (14) could come from any source, including analytic solutions or numerical models like MODPATH, MT3D, or RWHet, as long as the transport parameters do not change in time. In this sense, the analytic solutions (9) and (14) extend the methods of the popular code CXTFIT [29] to any time-homogeneous boundary value problem solved analytically or numerically. On the other hand, the exact stochastic process is given by exponential mobile and immobile times, with rates $\beta\lambda$ and λ, respectively, so that a simple, efficient, and accurate particle-tracking method can be used to simulate the mobile/immobile transport (Fig. 2b). Furthermore, it is a simple matter to extend these results to arbitrary waiting time densities as shown in the next example. Single-rate mass transfer adds two parameters to the classical ADE.

Linear retardation and single-rate mass transfer are now seen as very similar: both have exponential mobile times and exponential waiting times. In single-rate mass transfer, the mobile and intervening waits are uncorrelated, while they are perfectly correlated in linear retardation.

5.3. Power-law, infinite-mean waiting times

In the case of power-law waiting times in the immobile zone, where the jump intensity $\phi(t) = \gamma t^{-\gamma-1}/\Gamma(1-\gamma)$ for some $0 < \gamma < 1$ (Appendix), the memory function $g(t) = t^{-\gamma}/\Gamma(1-\gamma)$ is the inverse Laplace transform of $g(s) = s^{\gamma-1}$. The convolutions in (1) and (2) are fractional derivatives in time of order γ, recovering the fractal mobile/immobile model [31]. The memory function gives the exact rate at which immobile particles, which have rested for at least t time units, are re-entering the mobile phase. In the case of a classical space generator $A_x = -v\partial/\partial x + D\partial^2/\partial x^2$, analytical solutions of the fractal mobile/immobile equation for total flow can be obtained from (9) with $a(x,u) = (4\pi Du)^{-1/2}\exp\left(-(x-vu)^2/(4Du)\right)$ the classical ADE solution, as in Section 5.1, and $h(u,t) = \int_0^t (t-y)^{-\gamma}l(y,u)dy$ where $l(t,u) = u^{-1/\gamma}S(u^{-1/\gamma}t)$ is

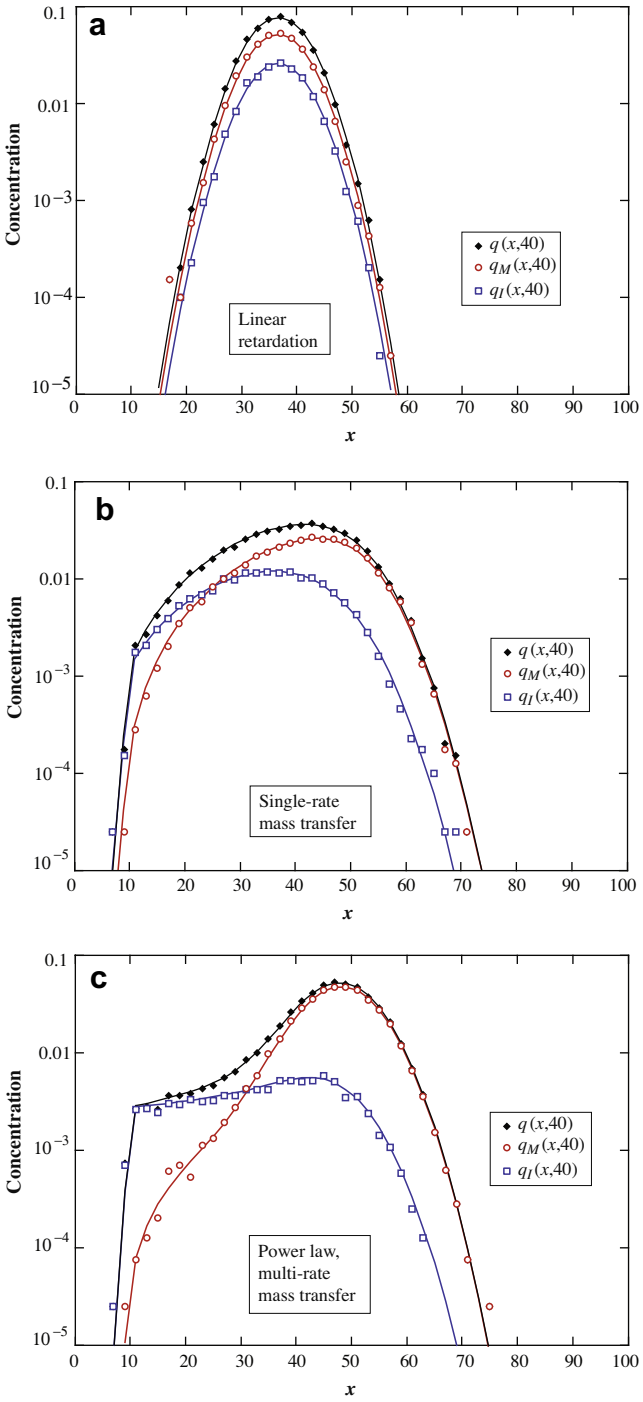

Fig. 2. Solutions for 1-d classical advection and dispersion with various forms of mass transfer: (a) linear retardation, (b) single-rate mass transfer, and (c) power-law mass transfer rates. In all cases, the transport parameters are $v = 1, D = 0.5, t = 40$ and $C_M(t=0) = \delta(x-10)$. Symbols are histograms of mobile, immobile, and total particles after tracking 20,000 initially mobile particles; curves are corresponding analytic solutions. In (a), $\lambda = 10$, $\beta = 0.5$, so $R = 1+\beta = 1.5$. In (b), the single-rate mass transfer parameters are $\beta = 0.5$ and $\lambda = 0.1$. In (c), mass transfer parameters are $\beta = 0.03$ and $\gamma = 0.5$.

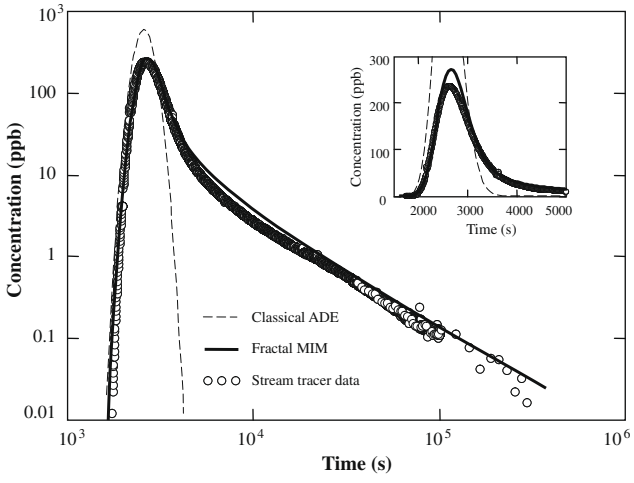

Fig. 3. Fit of the fractal MIM model to measured breakthrough [10] of Rhodamine WT after a transport distance of 306.4 m in a 2nd-order mountain stream. Figure from [31].

the probability density of a γ-stable subordinator, the inverse Laplace transform of $l(s,u) = e^{-us^\gamma}$. The function $S(t) = l(t,1)$ can be efficiently calculated using widely available numerical codes [24]. As well, the particle-tracking method uses exponential mobile times and power-law immobile times, matching the analytic methods [31] in all phases. The fractal MRMT adds two parameters to the classical ADE.

This model (Fig. 3) was used [31] to fit the heavy-tailed Rhodamine WT transport in a 2nd-order stream described by [10]. In this case, motion in the stream itself is described by the classical ADE with $v = 0.12$ m/ s and $D = 0.2$ m^2/s, while dye particles that move into the hyporheic zone are held relatively motionless for power-law random times with $\gamma = 0.3$ and $\beta = 0.0023$ s$^{-0.7}$.

6. Conclusions

The deterministic multi-rate mass transfer (MRMT) equations for modeling contaminant transport govern a subordinated Markov process with a mobile and an immobile state. We constructed a continuously evolving stochastic mobile/immobile (SMIM) process whose probability densities solve the mobile, immobile, and total concentration in the MRMT model. The link between the deterministic MRMT and SMIM models is made by requiring a particle to experience random times in the mobile state between immobile epochs. The mobile times are exponentially distributed. The memory function $g(t)$ in the MRMT is identified as proportional to the probability that a particle remains in the immobile state for a period greater than time t. It is also the rate at which particles, trapped in the immobile zone for a time greater than t, become mobile. Two simple algorithms are developed for coding the SMIM process into particle tracking codes. Several applications of the stochastic model illustrate the utility of the method and the link to previous continuum models of solute transport.

Appendix A. Extended MIM model

For some applications, the SMIM model of Section 3.1 is not sufficiently general. A more general model may be obtained by relaxing our assumptions on the waiting time variables and their scaling limit. Expand the Laplace symbol of the waiting time process $T(u)$ in the form

$$L(s) = s + \beta\lambda(1 - \psi_W(s)) = s + \beta\int_0^\infty (1 - e^{-st})\phi(t)dt,$$

where $\phi(t) = \lambda\psi_W(t)$ is called the jump intensity of the compound Poisson process $P(u) = W_1 + \cdots + W_{N(u)}$. Specifically, the number of jumps of size $a \leqslant t \leqslant b$ by operational time $u > 0$ is a Poisson random variable with mean $u\int_a^b \phi(t)dt$. Note that the total number of jumps of any size (take $a = 0$ and $b = \infty$) by operational time u is simply $N(u)$, a Poisson random variable with mean λu. In the general case, the jump intensity can increase to infinity as $t \to 0$, so long as the technical condition $\int_0^1 t\phi(t)dt < \infty$ is met. For example, heavy tailed waiting times with $P(W_i > t) \approx t^{-\gamma}$ in the immobile zone lead to a jump intensity $\phi(t) = \gamma t^{-\gamma-1}$ for $0 < \gamma < 1$. Then the Laplace symbol $L(s) = s + \beta L_W(s)$ where

$$L_W(s) = \int_0^\infty (1 - e^{-st})\phi(t)dt \tag{A.1}$$

for some jump intensity $\phi(t)$. Then $T(u) = u + W(u)$ where the density $l_W(t,u)$ of the immobile waiting time process $W(u)$ has Laplace transform $l_W(s,u) = e^{-u\beta L_W(s)}$. In the extended SMIM model, the FLT $q(k,s)$ of the SMIM process density is again given by (10), with $L(s) = s + \beta L_W(s)$. Then we arrive at the same equivalence between the SMIM and MRMT models, with $C_T(x,t) = q(x,t)$, if we equate $L(s) = s + \beta L_W(s) = s + s\beta g(s)$. Now the memory function has a more general interpretation

$$g(s) = \frac{1}{s}\int_0^\infty (1 - e^{-s\tau})\phi(\tau)d\tau = \int_0^\infty \int_0^\tau e^{-st}\,dt\phi(\tau)d\tau$$
$$= \int_0^\infty e^{-st}\int_t^\infty \phi(\tau)d\tau\,dt. \tag{A.2}$$

Inverting the LT shows that

$$g(t) = \Phi(t) = \int_t^\infty \phi(\tau)d\tau \tag{A.3}$$

the tail integral of the jump intensity. Note that $\Phi(t)$ is the rate of particle jumps out of the immobile zone, for particles that have remained immobile for at least t times units, and that (A.3) reduces to (12) if $\phi(t) = \lambda\psi_W(t)$. Generally speaking, since MRMT equations convolve the time derivative of concentration with the time integral of the jump intensity, a simple integration by parts converts those terms to a more physically meaningful convolution of concentration with jump intensity, which conveys that particles wait for a time τ in the immobile zone, and then release.

References

[1] Bear J. Dynamics of fluids in porous media. New York: Elsevier; 1972.
[2] Bochner S. Diffusion equations and stochastic processes. Proc Natl Acad Sci USA 1949;85:369–70.
[3] Brusseau ML, Jessup RE, Rao PSC. Modeling the transport of solutes influenced by multiprocess nonequilibrium. Water Resour Res 1989;25(9):1971–88.
[4] Carrera J, Sanchez-Vila X, Benet I, Medina A, Galarza G, Guimera J. On matrix diffusion: formulations, solution methods and qualitative effects. Hydrogeol J 1998;6(1):178–90.
[5] Çinlar E. Introduction to stochastic processes. Englewood Cliffs, New Jersey: Prentice-Hall; 1975.
[6] Coats KH, Smith BD. Dead-end pore volume and dispersion in porous media. Soc Pet Eng J 1964;4:73–84.
[7] Delay F, Bodin J. Time domain random walk method to simulate transport by advection–dispersion and matrix diffusion in fracture networks. Geophys Res Lett 2001;28(21):4051–4.
[8] Einstein A. On the theory of the Brownian movement. Ann Phys 1906;4(19):371–81.
[9] Feller W. An introduction to probability theory and its applications. Wiley series in probability and mathematical statistics, vol. II. New York: Wiley; 1971.
[10] Haggerty R, Wondzell SM, Johnson MA. Power-law residence time distribution in the hyporheic zone of a 2nd-order mountain stream. Geophys Res Lett 2002;29(13):1640. doi:10.1029/2002GL014743.
[11] Haggerty R, Gorelick SM. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. Water Resour Res 1995;31(10):2383–400.
[12] Haggerty R, McKenna SA, Meigs LC. On the late-time behavior of tracer test breakthrough curves. Water Resour Res 2000;36(12):3467–79.
[13] Hassan AE, Mohamed MM. On using particle tracking methods to simulate transport in single-continuum and dual continua porous media. J Hydrol 2002;275:242–60.
[14] Kinzelbach W. The random walk method in pollutant transport simulation. In: Custodio E et al., editors. Groundwater flow and quality modelling. Reidel Publishing Company; 1988. p. 227–45.
[15] LaBolle EM, Fogg GE, Tompson AFB. Random-walk simulation of transport in heterogeneous porous media: local mass-conservation problem and implementation methods. Water Resour Res 1996;32(3):583–93.
[16] LaBolle EM, Quastel J, Fogg GE, Gravner J. Diffusion processes in composite porous media and their numerical integration by random walks: generalized stochastic differential equations with discontinuous coefficients. Water Resour Res 2000;36(3):651–62.
[17] Liu HH, Bodvarsson GS, Pan L. Determination of particle transfer in random walk particle methods for fractured porous media. Water Resour Res 2000;36(3):707–13.
[18] Magdziarz M, Weron A, Weron K. Fractional Fokker–Planck dynamics: stochastic representation and computer simulation. Phys Rev E 2007;75:016708.
[19] Maxwell RM, Welty C, Harvey RW. Revisiting the Cape Cod bacteria injection experiment using a stochastic modeling approach. Environ Sci Technol 2007;41:5548–58.
[20] Meerschaert MM, Benson DA, Bäumer B. Multidimensional advection and fractional dispersion. Phys Rev E 1999;59(5):5026–8. doi:10.1103/PhysRevE.59.5026.
[21] Meerschaert MM, Scheffler H-P. Limit theorems for continuous time random walks with infinite mean waiting times. J Appl Probab 2004;41:623–38.
[22] Meerschaert MM, Scheffler H-P. Triangular array limits for continuous time random walks. Stoch Proc Appl 2008;118(9):1606–33.

[23] Michalak AM, Kitanidis PK. Macroscopic behavior and random-walk particle tracking of kinetically sorbing solutes. Water Resour Res 2000;36(8):2133–46.
[24] Nolan JP. Numerical calculation of stable densities and distribution functions, heavy tails and highly volatile phenomena. Commun Statist Stoch Models 1997;13(4):759–74.
[25] Painter S, Cvetkovic V, Mancillas J, Pensado O. Time domain particle tracking methods for simulating transport with retention and first-order transformation. Water Resour Res 2008;44:W01406. doi:10.1029/2007WR005944.
[26] Salamon P, Fernàndez-Garcia D, Gómez-Hernández JJ. A review and numerical assessment of the random walk particle tracking method. J Contam Hydrol 2006;87:277–305.
[27] Salamon P, Fernàndez-Garcia D, Gòmez-Hernàndez JJ. Modeling mass transfer processes using random walk particle tracking. Water Resour Res 2006;42:W11417. doi:10.1029/2006WR004927.
[28] Tompson AFB, Gelhar LW. Numerical simulation of solute transport in three-dimensional, randomly heterogeneous porous media. Water Resour Res 1990;26(10):2541–62.
[29] Toride N, Leij FJ, van Genuchten MTh. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, v. 2.0. Research Report No. 137. US Salinity Laboratory, U.S.D.A., A.R.S. Riverside, CA, 1995.
[30] Schumer R, Benson DA, Meerschaert MM, Baeumer B. Multiscaling fractional advection–dispersion equations and their solutions. Water Resour Res 2003;39(1):1022. doi:10.1029/2001WR001229.
[31] Schumer R, Benson DA, Meerschaert MM, Baeumer B. Fractal mobile/immobile solute transport. Water Resour Res 2003;39(10):1296. doi:10.1029/2003WR002141.
[32] Valocchi AJ, Quinidoz HAM. Application of the random walk method to simulate the transport of kinetically adsorbing solutes. In: Abriola LM, editor. Groundwater contamination. IAHS Publ. No. 185, 1989. p. 35–42.
[33] van Genuchten MT, Wierenga PJ. Mass transfer studies in sorbing porous media, 1. Analytical solutions. Soil Sci Soc Am J 1976;40:473–80.
[34] Weissmann GS, Zhang Y, LaBolle EM, Fogg GE. Dispersion of groundwater age in alluvial aquifer system. Water Resour Res 2002;38(10). doi:10.1029/2001WR000907. Art. No. 1198.
[35] Zhang Y, Benson DA, Meerschaert MM, Scheffler HP. On using random walks to solve the space-fractional advection–dispersion equations. J Stat Phys 2006;123(1):89–110.
[36] Zhang Y, Benson DA, Meerschaert MM, LaBolle EM, Scheffler HP. Random walk approximation of fractional-order multiscaling anomalous diffusion. Phys Rev E 2006;74:026706.
[37] Zhang Y, Benson DA, Baeumer B. Predicting the tails of breakthrough curves in regional-scale alluvial systems. Ground Water 2007;45(4):473–84. doi:10.1111/j.1745-6584.2007.00320.x.
[38] Zhang Y, Benson DA. Lagrangian simulation of multidimensional anomalous transport at the MADE site. Geophys Res Lett 2008;35:L07403. doi:10.1029/2008GL033222.