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AUTHORS: *G. Srinivasan, D.M. Tartakovsky, M. Dentz, H. Viswanathan, B. Berkowitz, B.A. Robinson*

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Random Walk Particle Tracking Simulations of Non-Fickian Transport in Heterogeneous Media

G. Srinivasan[a], D. M. Tartakovsky[b], M. Dentz[c], H. Viswanathan[d], B. Berkowitz[e], B. A. Robinson[d]

[a] *Theoretical Division, Los Alamos National Laboratoty, Los Alamos, NM 87545, USA.*
[b] *Department of Mechanical and Aerospace Engineering, University of California, San Diego, 9500 Gilman Drive, Mail Code 0411, La Jolla, CA 92093, USA*
[c] *Institute of Environmental Assessment and Water Research (IDÆA-CSIC), Barcelona, Spain*
[d] *Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico, USA*
[e] *Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, Rehovot, Israel*

Abstract

Derivations of continuum nonlocal models of non-Fickian (anomalous) transport require assumptions that might limit their applicability. We present a particle-based algorithm, which obviates the need for many of these assumptions by allowing the stochastic processes representing the spatial and temporal random increments to be correlated in space and time, stationary or non-stationary, and to have arbitrary distributions. The approach treats a particle trajectory as a subordinated stochastic process that is described by a set of Langevin equations, which represent a continuous time random walk (CTRW). A convolution-based particle tracking (CBPT) is used to increase the computational efficiency and accuracy of these particle-based simulations. The combined CTRW-CBPT approach enables one to convert any particle-tracking legacy code into a simulator capable of handling non-Fickian transport.

Keywords: random walk, particle tracking, anomalous transport

Email addresses: gowri@lanl.gov (G. Srinivasan), dmt@ucsd.edu (D. M. Tartakovsky), marco.dentz@idaea.csic.es (M. Dentz)

1. Introduction

Many physical, biological, and biochemical phenomena [e.g., 1, 2, 3, 4] involve a combination of three passive transport mechanisms: advection, molecular diffusion, and hydrodynamic dispersion. Standard mathematical descriptions of such phenomena rely on an advection-dispersion equation (ADE),

$$\frac{\partial c}{\partial t} = \nabla \cdot (\mathbf{D} \nabla c) - \nabla \cdot (\mathbf{v} c), \tag{1}$$

where c is the volumetric concentration of a substance (e.g., solute), $\mathbf{v}$ is the (macroscopic) advection velocity, and $\mathbf{D} = D_m \mathbf{I} + \mathbf{D}_d$ is the dispersion coefficient tensor defined as the sum of the molecular diffusion coefficient D_m ($\mathbf{I}$ being the unit tensor) and the dispersivity tensor $\mathbf{D}_d = \mathbf{D}_d(\mathbf{v})$. Although the ADE proved to be indispensable in describing many transport processes, it has a number of drawbacks and limitations that are both computational and conceptual in nature.

Numerical solutions of the ADE (1) introduce "numerical dispersion", which manifests itself in excessive smearing of concentration profiles at large Péclet numbers. This problem is exacerbated by high degrees of anisotropy that often characterize hydrodynamic dispersion. For example, transport in natural porous media typically exhibit longitudinal dispersivities that are two orders of magnitude higher than their transverse counterparts [5]. Numerical dispersion can be controlled by employing Eulerian-Lagrangian [6, 7] and other [8] algorithms, many of which are computationally expensive.

A more fundamental shortcoming of the macroscale ADE (1) is its inability to capture anomalous or non-Fickian transport behavior, which is often observed in heterogeneous environments [9, 10, 11, 12, 13, 14]. This failure can be attributed to subgrid-scale heterogeneity that is not resolved at the support scale on which the parameters of the ADE are defined. If it is possible to resolve the heterogeneity structure on all scales, the corresponding ADE reflects the related anomalous transport behavior [e.g., 15]. This is not very realistic for many practical applications.

This shortcoming of the macroscale ADE can be effectively overcome by replacing the ADE (1) with its counterparts that are *nonlocal* in space and/or time. Derivations of nonlocal transport equations rely on a number of assumptions. For example, stochastic derivations of nonlocal mean transport equations often require velocity fluctuations to be either small [16] or Gaussian [17]; and standard derivations of both fractional ADEs (fADEs) [18, 19]

and effective equations of continuous time random walk (CTRW) models [20, 21, 22, 23, 24] are based on the assumption that subgrid scale fluctuations are space-time stationary. Particle-based simulations provide a computationally efficient framework for solving both local and nonlocal effective transport equations. Particle-tracking algorithms (PTAs) are used routinely to control numerical dispersion in solutions of the ADE (1) [25, 26, 27, 28, 29] and, more recently, to solve nonlocal effective transport equations based on CTRW [30, 31, 32, 33], fADE [34], and multirate mass transfer [35, 36]. Advantages and disadvantages of using PTAs to solve the ADE (1), e.g., the challenges posed by local mass conservation and a large number of particles that are needed to obtain smooth concentration profiles, are discussed in [37]. Solving nonlocal effective models with PTAs does not relax the assumptions that are required for their derivation.

We introduce a particle-based approach for modeling non-Fickian (anomalous) transport in heterogeneous environments that requires no assumption about statistical properties of the model parameters. To increase the computational efficiency and accuracy of the particle-based simulations, we employ the convolution-based particle tracking (CBPT) method [38]. An added benefit of the proposed approach lies in its ability to convert any existing (legacy) particle-tracking code into a simulator capable of handling non-Fickian behavior.

Particle tracking algorithms for solving the ADE (1) utilize its equivalence to the Langevin equation, which describes a solute particle's trajectory as a stochastic process [39]. Introducing a randomized time step into this process yields a new "subordinated" stochastic process that is capable of capturing anomalous transport behavior [e.g., 40]. This subordinated process is described by a set of Langevin equations, which represent a CTRW [e.g., 41]. In this paper, we adopt a general Langevin approach that imposes no statistical restrictions on the stochastic processes representing the spatial and temporal random increments. Each of these two processes can be correlated, non-stationary, and cross-correlated with the other, as well as have arbitrary distributions.

Employing this subordination strategy, we obtain a simple method to convert any random walk particle-tracking simulator into a continuous time random walk simulator. This enables us to achieve two computational advantages. First, the proposed approach is non-intrusive in that it allows one to use any existing particle tracking simulator for modeling non-Fickian behavior. Second, the proposed approach is applicable to heterogeneous and non-

stationary fields, whereas standard continuum formulations of non-Fickian transport require stationarity and statistical homogeneity. For stationary and uncorrelated random increments the well known partial differential equation (PDE) formulations of CTRW in terms of generalized Fokker-Planck equations [23] can be obtained by a generalized Kramers-Moyal expansion [e.g., 42]. The two components of the proposed approach, CBPT and CTRW, are described in Sections 2 and 3, respectively. The computational algorithm is presented in Section 3.1. Section 4.1 contains a computational example that can be solved analytically and, hence, is used to analyze the accuracy and robustness of our algorithm. In Section 4.2, we apply the algorithm to model non-Fickian transport in two separate three-dimensional macroscopically heterogeneous porous media; the simulation results are contrasted with those obtained by solving the classical ADE (1). Section 5 provides a brief summary of the results and conclusions.

2. Convolution-Based Particle Tracking (CBPT)

A standard random walk particle tracking [e.g., 28] solves the ADE (1) based on the equivalence of the ADE and the following Langevin equation [e.g., 39]

$$\mathbf{X}(t+\Delta t) = \mathbf{X}(t) + \mathbf{A}[\mathbf{X}(t)]\Delta t + \mathbf{B}[\mathbf{X}(t)] \cdot \boldsymbol{\xi}\sqrt{\Delta t}. \tag{2}$$

Here $\mathbf{X}(t) = [X_1(t), X_2(t), X_3(t)]^T$ is the random particle location at time t, $\boldsymbol{\xi} = [\xi_1, \xi_2, \xi_3]^T$ is Gaussian white noise with zero mean and unit variance,

$$\langle \xi_i \rangle = 0, \qquad \langle \xi_i \xi_j \rangle = \delta_{ij} \tag{3}$$

The drift vector $\mathbf{A}$ and the second-order tensor $\mathbf{B}$ are related to the coefficients in (1) by [e.g., 25]

$$\mathbf{A} = \mathbf{v} + \nabla \mathbf{D}, \qquad \mathbf{B}\mathbf{B}^T = 2\mathbf{D}. \tag{4}$$

The particle's initial position, or its label, is given by $\mathbf{X}(t=0) = \mathbf{x}_0$.

The CBPT [38] accelerates the convergence of the particle-tracking algorithm (2)–(4), i.e., requires fewer particles, by taking advantage of the linearity of the ADE (1). Let $g(\mathbf{x}, t-\tau|\mathbf{x}_0)$ denote the Green's function for (1), which is defined as a solution of the adjoint equation

$$\frac{\partial g}{\partial \tau} = \nabla \cdot (\mathbf{D}\nabla g) + \mathbf{v} \cdot \nabla g, \tag{5}$$

subject to the initial condition $g(\mathbf{x}, \tau = t|\mathbf{x}_0) = \delta(\mathbf{x} - \mathbf{x}_0)$ and appropriate homogeneous boundary conditions. The Green's function $g(\mathbf{x}, t|\mathbf{x}_0)$ can be expressed in terms of particle trajectories as [e.g., 39]

$$g(\mathbf{x}, t|\mathbf{x}_0) = \langle \delta \left[\mathbf{x} - \mathbf{X}(t)\right] \rangle |_{\mathbf{X}(0)=\mathbf{x}_0}, \tag{6}$$

where the angular bracket denotes the ensemble average over the random vector $\boldsymbol{\xi}$. We use the particle tracking algorithm (2) and (6) to compute the Green's function $g(\mathbf{x}, t - \tau|\mathbf{x}_0)$.

Concentration $c(\mathbf{x}, t)$ resulting from spatially and/or temporally distributed sources $\dot{m}(\mathbf{x}', t')$ can now be computed as

$$c(\mathbf{x}, t) = \int_0^t \int_\Omega \dot{m}(\mathbf{x}_0, \tau) g(\mathbf{x}, t - \tau|\mathbf{x}_0) \mathrm{d}\mathbf{x}_0 \mathrm{d}\tau, \tag{7}$$

where Ω is the computational domain. The accuracy and computational efficiency of the CBPT (2), (6), and (7) are analyzed in detail in [38]. For the computational example described in Section 4.1, the performance of the CBPT algorithm is demonstrated in Table 1.

Number of particles	Duration of mass injection (Years)	CBPT method, ϵ	Conventional method, ϵ
10^5	1000	0.0154	0.433
10^5	100	0.0301	0.177
10^5	10	0.0698	0.0925
10^5	1	0.122	0.119

Table 1: Performance metrics for the CBPT and conventional particle-tracking methods.

The performance metric ϵ in Table 1 is defined as

$$\epsilon = \frac{1}{N} \sqrt{\sum_{i=1}^{N} \left[\frac{c_{\mathrm{ex}}(\mathbf{x}_i) - c_{\mathrm{nu}}(\mathbf{x}_i)}{c_{\mathrm{ex}}(\mathbf{x}_i)} \right]^2}, \tag{8}$$

where c_{ex} is the "exact" concentration computed with an analytical solution, c_{nu} is the concentration predicted by a numerical method, i.e., by either the CBPT or the conventional particle tracking method, and N is the number of observations. It can be seen that the CBPT method is always at least

as accurate as the conventional particle tracking methods and needs fewer particles to achieve the same accuracy in most cases, especially for larger solute injection times. The concentration as a function of distance from the center of the plume is plotted in Figure 1.

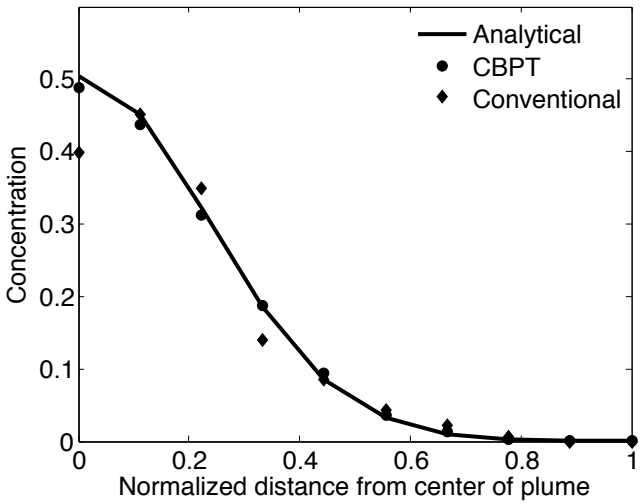

Figure 1: Concentration $c(x_1, t)$ at time $t = 1000$ y predicted with the analytical solution, the conventional particle-tracking method, and the CBPT.

3. Continuous Time Random Walk (CTRW)

The random walk model (2)–(4) treats the time step $\tau \equiv \Delta t$ as deterministic and the transition-length vector $\boldsymbol{\xi}$ as random, which results in Fickian dispersion. Let us introduce the randomized or operational time $s(t)$ [e.g., 40] defined as a "renewal process" [e.g., 43, 44] that is conjugate to

$$\frac{\mathrm{d}t(s)}{\mathrm{d}s} = \tau(s), \tag{9}$$

where $\tau(s)$ is a random process to be specified below. The random trajectory becomes an implicit function of time, $\mathbf{X}[s(t)]$. Thus, we obtain the subordinated system of Langevin equations [e.g., 41]

$$\mathbf{X}(s_n + \Delta s) = \mathbf{X}(s_n) + \mathbf{A}[\mathbf{X}(s_n)]\Delta s + \mathbf{B}[\mathbf{X}(s_n)] \cdot \boldsymbol{\xi}(s_n)\sqrt{\Delta s} \tag{10a}$$

$$t(s_n + \Delta s) = t(s_n) + \tau(s_n)\Delta s, \tag{10b}$$

where $\mathbf{A}$ and $\mathbf{B}$ are defined in (4), Δs is the constant increment of the discretized operational time $s_n = n\Delta s$. In general, the random series $\{\boldsymbol{\xi}(s_n)\}$ and $\{\tau(s_n)\}$ can be correlated or uncorrelated, stationary or nonstationary, and have arbitrary distributions. As pointed out in the Introduction, this formulation is quite general and provides an alternative to PDE formulations of CTRW that assume statistical stationarity and independence of the stochastic processes $\{\boldsymbol{\xi}(s)\}$ and $\{\tau(s)\}$. Furthermore, note that PDE formulations in terms of non-local Fokker-Planck equations typically rely on the truncation of a Kramers-Moyal expansion after the second-order term [e.g., 39, 21]. The validity of this truncation in the CTRW framework for a Gaussian white noise $\{\boldsymbol{\xi}(s)\}$ has been demonstrated in [30] by using random walk particle tracking simulations.

To facilitate the comparison with the existing CTRW literature, in the following we take each of the processes $\{\boldsymbol{\xi}(s)\}$ and $\{\tau(s)\}$ to be uncorrelated and characterized by the joint probability density

$$\mathcal{P}\left[\{\boldsymbol{\xi}(s_n);\tau(s_n)\}_{n=1}^{N}\right] = \prod_{n=1}^{N} \psi[\boldsymbol{\xi}(s_n),\tau(s_n)], \tag{11}$$

where $\psi(\boldsymbol{\xi},\tau)$ is the joint transition length and time distribution density. The principal of causality requires that the temporal random process satisfy the condition $t(s_{n+1}) \geq t(s_n)$, which implies that $\tau(s_n) \geq 0$. The system of Langevin equations (10) describes particle motion as a CTRW in a macroscopically heterogeneous medium.

The choice of the probability density $\psi(\boldsymbol{\xi},\tau)$ is crucial to simulating non-Fickian transport in (randomly) heterogeneous environments, which are characterized by evolving hierarchies of length scales.

Some approaches and criteria for computing or selecting $\psi(\boldsymbol{\xi},\tau)$ can be found in [e.g., 45, 22]. Here we consider random walks that are mutually uncorrelated in space and time, so that the joint probability density $\psi(\boldsymbol{\xi},\tau)$ can be decoupled, i.e., $\psi(\boldsymbol{\xi},\tau) = \psi_s(\boldsymbol{\xi})\psi_t(\tau)$.

Furthermore, in the following we assume that transition times on a deterministic time interval $[t_1, t_2]$ follow a truncated power-law distribution [e.g., 30, 46]

$$\psi_t(\tau) = \frac{r^{\beta}(1+\tau/t_1)^{-1-\beta}}{t_1\Gamma(-\beta,r)}\,\mathrm{e}^{-r-\tau/t_2}, \qquad r = \frac{t_1}{t_2}, \qquad 0 \leq \beta \leq 2, \tag{12}$$

where $\Gamma(a,x)$ is the incomplete Gamma function. The median transit time is set equal to the increment of the operational time, $t_1 = \Delta s$. For times $\tau > t_2$, $\psi_t(\tau)$ decreases exponentially fast. The transport behavior is anomalous in the transition regime $t_1 \leq t \leq t_2$ and becomes Fickian for large times $t > t_2$.

3.1. Simulation Algorithm

The Green's function $\overline{g}(\mathbf{x}, t|\mathbf{x}_0)$ is given in terms of the particle trajectories of the CTRW (10) by

$$\overline{g}(\mathbf{x}, t|\mathbf{x}_0) = \langle \delta\{\mathbf{x} - \mathbf{X}[s(t)]\}\rangle|_{\mathbf{X}(0)=\mathbf{x}_0}, \tag{13}$$

where the angular brackets denote the average over the spatial and temporal random processes $\{\boldsymbol{\xi}(s)\}$ and $\{\tau(s)\}$. Note that the particle trajectory here is an implicit function of time, $\mathbf{X}(t) \equiv \mathbf{X}[s(t)]$. Expression (13) can be written as

$$\overline{g}(\mathbf{x}, t|\mathbf{x}_0) = \int_0^\infty \mathrm{d}s \langle \delta[\mathbf{x} - \mathbf{X}(s)]\delta[s - s(t)]\rangle|_{\mathbf{X}(0)=\mathbf{x}_0}. \tag{14}$$

We discretize the operational time s according to $s_n = n\Delta s$ and $s(t) = N_t \Delta s$, where the discrete process N_t is defined by

$$N_t = \min(n|t(s_{n+1}) > t) \tag{15}$$

Thus, we obtain for $\overline{g}(\mathbf{x}, t|\mathbf{x}_0)$ the expression [e.g., 47]

$$\overline{g}(\mathbf{x}, t|\mathbf{x}_0) = \sum_{n=0}^{\infty} \langle \delta[\mathbf{x} - \mathbf{X}(s_n)]\delta_{n,N_t}\rangle|_{\mathbf{X}(0)=\mathbf{x}_0} = \langle \delta[\mathbf{x} - \mathbf{X}(s_{N_t})]\rangle|_{\mathbf{X}(0)=\mathbf{x}_0}. \tag{16}$$

This relation provides a straightforward recipe on how to obtain $\overline{g}(\mathbf{x}, t)$. The solution for the concentration profile for a general source distribution then is calculated by the convolution of the cource term with $\bar{g}$ as expressed by (7). The corresponding algorithm combines the CBPT and CTRW approaches and consists of the following steps.

1. Starting from a point source at $\mathbf{x}_0$ at time $t = 0$, the spatio-temporal particle trajectories are tracked according to (10). After N_t steps, that is, when the simulation time t is between t_N and t_{N+1}, $t_N \leq t < t_{N+1}$, the position $\mathbf{x}_N$ is recorded. The Green's function $\bar{g}$ is determined by sampling the particle positions in space according to (16).

2. Finally, the anomalous concentration profile is obtained by convolving $\bar{g}$ with the source term.

This algorithm renders itself to straightforward integration into most existing legacy codes, as we do below for the DOE-certified code Finite Element Heat and Mass Transfer Code (FEHM) [48]. Next, we apply this code to three computational examples of increasing difficulty. The example in Section 4.1 is used to demonstrate the accuracy and computational efficiency of the CBPT. Section 4.2 provides two examples of the use of the CBPT-CTRW to model anomalous transport in realistic three-dimensional geological settings.

3.2. Integration Into Legacy Codes

FEHM is is multiphase, multidimensional reservoir simulator. In order to calculate the velocity field, FEHM simulations may include numerous coupled processes including thermo-hydro-chemical-mechanical (THCM). These coupled processes are often important for studies of carbon sequestration, nuclear waste disposal, and hazardous waste disposal. It currently lacks the capability of handling anomalous transport. It relies on a three-dimensional node based particle tracking method that takes advantage of the fluxes at nodes being given by the flow solution, and can be used easily with unstructured grids etc, without having to use interpolation schemes. By using the velocity field from the flow simulation, the particle tracking algorithm takes advantage of the complex velocity field calculated by the flow simulation that often depends on the numerous coupled processes mentioned above. The proposed algorithm can be used with any node based particle tracking technique.

4. Transport in Macroscpically Homogeneous and Heterogeneous Media

In this section, we apply the random walk algorithm presented above to transport in macroscopically homogeneous and heterogeneous media. The code is validated against known solutions for instantaneous sources in macroscopically homogeneous media [30] and applied to solute transport evolving from continuous solute injections in macroscopically homogeneous and heterogeneous media.

4.1. Macroscopically Homogeneous Medium

Consider solute transport in a three-dimensional macroscopically homogeneous porous medium $\Omega = [0, \infty] \times [0, L_2] \times [0, L_3]$. Flow velocity $\mathbf{v}$ is taken to be constant and aligned with the x_1 coordinate axis, $\mathbf{v} = [v, 0, 0]^T$ with $v = 34.2$ m/y. The longitudinal dispersivity is set to $\alpha_L = 500$ m, the corresponding longitudinal dispersion coefficient is $D_L = \alpha_L v$, and the transverse horizontal and vertical dispersion are neglected, $D_T = 0$. Constant head boundaries are prescribed at the inlet and outlet, with a difference in head of 0.377 MPa. The porosity and permeability are constant throughout the medium with values of $\omega = 0.03361$ and $k = 10^{-12}$ m^2, respectively. The parameters are chosen such that the resulting flow translates into a mean travel time of 500 y to reach the outlet. Regardless of the transport model used, this parameter choice renders transport one-dimensional, $c(\mathbf{x}, t) = c(x_1, t)$.

The initial concentration is set to $c(x_1, t = 0) = 0$. The boundary condition at $x_1 = 0$ is more conveniently expressed in terms of the flux-averaged concentration [49]

$$c_f(x_1, t) = v^{-1} \int_0^{x_1} \frac{\partial c(x_1', t)}{\partial t} \mathrm{d}x_1'. \tag{17}$$

At the inlet $x_1 = 0$, $c_f(x_1, t)$ is given by

$$c_f(x_1 = 0, t) = j(t)/v, \tag{18}$$

where $j(t)$ is the boundary flux. The concentration and concentration flux are zero at the boundary at infinity. We study transport in terms of spatial profiles, that is snapshots of $c(x_1, t)$ and breakthrough curves at a given distance. The latter are equivalent to first passage time distributions at a control plane. They are obtained from the flux-averged concentration. In these simulations, the domain Ω is discretized with grid spacings $\Delta x_1 = 400$ m.

4.1.1. Validation of the Simulation Algorithm

Here, we validate the simulation algorithm against known solutions for the flux-averaged concentration $c_f(x_1, t)$ with a constant, continuous injection at the inlet, that is, $j(t) = v$ at $x_1 = 0$ using a total of 10^4 particles. For stationary and uncorrelated random increments, the CTRW (10) admits a

PDE representation in terms of a temporally non-local Fokker-Planck equation [e.g., 23, 21, 30]. Dentz et al. [30] studied resident and flux-averaged concentrations for anomalous transport in a macroscopically homogeneous medium using random walk simulations as well as Laplace space solutions of the equivalent generalized Fokker-Planck equations. For the above specified boundary and initial conditions, they provide for the Laplace transform of the flux-averaged concentration the following expression

$$\tilde{c}_f(\lambda, x_1) = \exp\left[-\frac{v x_1}{2D_L}\left(\sqrt{1+4\frac{\lambda D_L}{\tilde{M} v^2}}-1\right)\right]. \tag{19a}$$

Here the tilde indicates Laplace transforms, λ is the Laplace variable, $\tilde{M}$ is the Laplace transform of the memory function defined as

$$\tilde{M}(\lambda) = \frac{t_1 \lambda \tilde{\psi}_t(\lambda)}{1-\tilde{\psi}_t(\lambda)} \tag{19b}$$

and $\tilde{\psi}_t(\lambda)$ is the Laplace transform of $\psi_t(t)$ in (12). The Laplace transform of the concentration $c(x_1, t)$ given by a solution of the ADE (1) is recovered from (19a) by setting $\tilde{M} \equiv 1$.

The analytical solution (19) is used to analyze the convergence of the CBPT and to validate the particle tracking implementation of the CTRW (10a)–(12) (the simulation algorithm in Section 3.1). Figure 2 compares the accuracy of the CBPT for both classical (Fig 2a) and anomalous (Fig 2b) transport. In the latter case, the CBPT is an integral part of the CBPT-CTRW algorithm described in Section 3.1. In both cases, the Laplace transform (19) of concentration for the analytical solution is inverted with the algorithm of de Hoog [50].

The breakthrough is computed at a distance of $x = 15.2$ km over a total time of 3000 y. The results from both analytical and numerical (the CBPT-CTRW algorithm) simulations are plotted in Figure 2 for the ADE and $\beta = 1.25$. The analytical solutions shown as circles and the numerical solutions represented by solid lines are in excellent agreement with each other. Such continuous injection scenarios are of practical importance for the modeling of contamination events in industrial plants, where contaminants can leak into the subsurface over many years, underground nuclear waste storage, as well as for the modeling of heat plumes in the subsurface that are generated by heat exchangers.

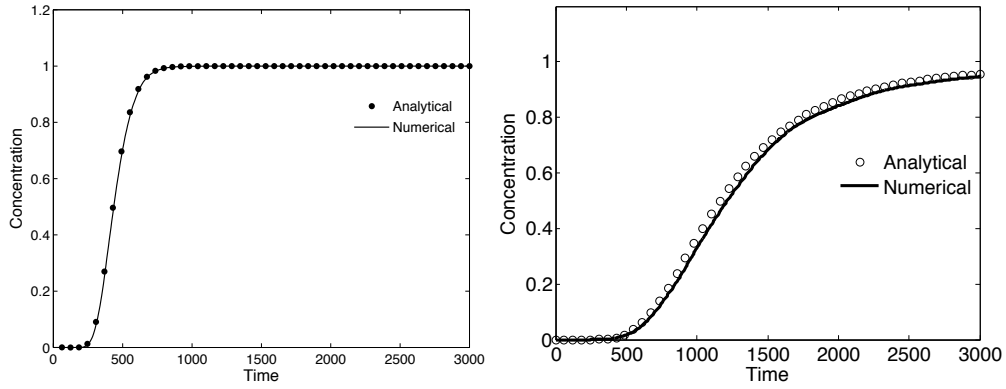

Figure 2: The breakthrough curves at $x_1 = 15.2$ km predicted with (a) the classical and (b) anomalous ($\beta = 1.25$) models of transport.

4.1.2. Breakthrough Curves and Spatial Profiles

An often neglected aspect of contaminant transport is the spatial nature of the plume across the entire field of study, since PTAs are mostly concerned with the breakthrough across a control plane. In this section, we present both breakthrough curves as well as the spatial concentration distribution for pulse injection $j(t) = v\delta(t)$ at the inlet $x_1 = 0$.

As in [30], we study the the effects on anomalous transport of the three key parameters in the CTRW model defined by the truncated power-law waiting time distribution (12): the median waiting time t_1, the cut-off time t_2 after which transport becomes Fickian, and the exponent β.

Consequently, we set $t_1 = 4$ y and $t_2 = 10^4$ y, and focus on the effects of $0 \leq \beta \leq 2$. It has been shown [e.g., 22] that $\beta = 2$ asymptotically leads to the Fickian behavior as predicted with the ADE (1) and that deviations from the Fickian transport become stronger as β becomes smaller.

Figure 3 depicts the breakthrough curves resulting from the pulsed boundary condition, $c(0,t) \equiv 1$ for $t \leq 10^3$ y and $c(0,t) \equiv 0$ for $t > 10^3$ y. The breakthroughs computed with the particle tracking simulations of the classical and anomalous transport are shown for several values of β.

In accordance with the theory, $\beta = 2$ gives rise to the classical transport behavior in terms of breakthrough times, peak concentrations, and Gaussianity of concentration profiles. As β decreases, breakthrough times become larger and concentration profiles exhibit progressively longer tails. The peak breakthrough values of concentration become progressively smaller, since the area under the breakthrough curves (i.e., total mass) is constant. The num-

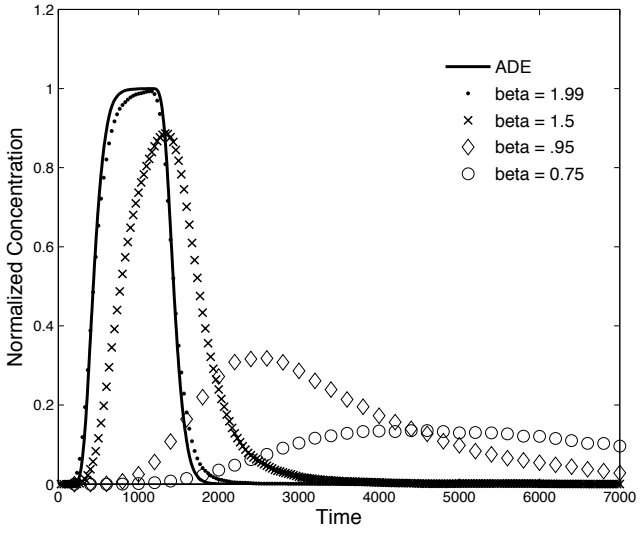

Figure 3: Breakthrough curves of concentration $c(x_1, t)$ at $x_1 = 15.2$ km for the pulsed input at the inlet $x_1 = 0$.

ber of particles that is required to represent breakthrough curves within a given tolerance level increases as β decreases and the deviation from the Gaussian behavior becomes more pronounced.

Figure 4 exhibits the temporal evolution of the concentration profiles for several values of β. The classical transport model (ADE or $\beta = 2$) exhibits no tailing and predicts that the solute occupies the entire computational domain by $t = 2000$ y. For $\beta = 1.99$, the tailing is very small and most of the mass has broken through by $t = 2000$ y and all of it by $t = 3000$ y. While $\beta = 1.5$ leads to a significant tailing, the arrival at the outlet starts to taper off by 2000 y. The concentration profiles corresponding to $\beta < 1$ indicate that mass is still breaking through at the end of the simulation time.

Figure 4 also reveals that the concentration at the inlet $x_1 = 0$ increases with decreasing β. This is because smaller values of β correspond to larger residence times in a boundary cell, resulting in a slower rate of transport across the medium and hence later arrival at the cross-section $x_1 = 15.2$ km. This is a mathematical representation of subscale mass transfer processes, such as diffusion into dead-end pores, which retard the solute migration.

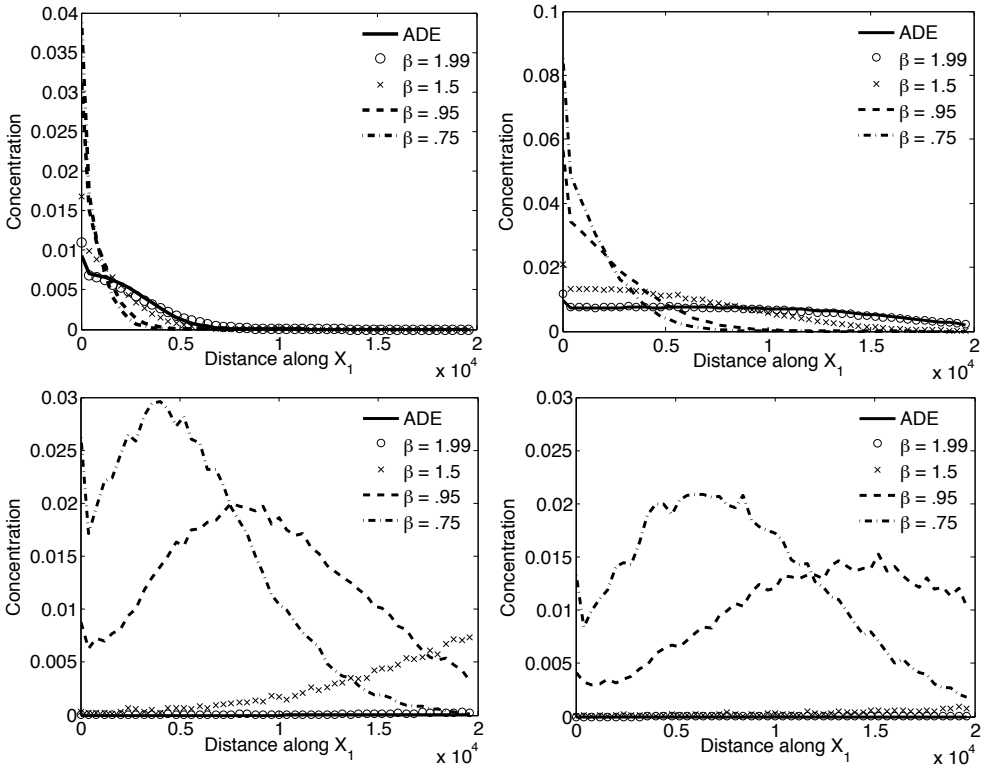

Figure 4: Concentration profiles $c(x,t)$ at (a) $t = 100$ y, (b) $t = 500$ y, (c) $t = 2000$ y, and (d) $t = 3000$ y for pulsed input at the inlet

4.2. Macroscopically Heterogeneous Medium

We use the CBPT-CTRW algorithm to simulate anomalous transport in heterogeneous media using two examples presented here. We consider in both examples, a three-dimensional heterogeneous porous medium $\Omega = [0, L_1] \times [0, L_2] \times [0, L_3]$. The simulation results presented below correspond to $L_1 = 20$ km, $L_2 = 9.6$ km and $L_3 = 5$ km.

In the first example, the model was divided into 4 equal zones in the primary flow direction, spanning $5km$ each. The initial zone and final zone have the same properties as the homogeneous media example of the previous section. The second zone has a reduced porosity of $\omega = 0.01425$ and the third zone a reduced permeability of $k = 10^{-13}$ m^2. The simulations below correspond to $H_1 - H_2 = 0.377$ MPa. The rest of the boundaries are impermeable to flow. To solve the flow equation (20) with the finite element code FEHM, the domain is discretized with a total of $51 \times 25 \times 101 = 128,775$ nodes in the x_1, x_2, and x_3 directions, respectively. The transport equations were solved using 10^4 particles.

Lower porosities result in faster movement of particles through zone 2. The overall flow is slower, as a result of the lower permeability across one of the four zones, since the effective permeability is a harmonic mean of the different permeability values. The breakthrough point for these simulations was at $L_1 = 15.2km$. The simulation was performed for 3000 years and tracer injected continuously for the entire length of the simulation. The Breakthrough Curve (Fig 5) is shown for the ADE as well as for the case of $\beta = 1.25$.

This example demonstrates the effects of large scale heterogeneity on contaminant transport. Features such as high permeability faults or low permeability clay lenses can be represented in this manner.

In the second example, we take a geostatistical approach for representing heterogeneity. In the subsurface, permeability distributions often follow a log-normal permeability distribution and are correlated. If large scale features are not present or known, a log-normal permeability distribution is often used simulate the structure of the permeability field. The mean, variance, and correlation length are quantities that can be obtained from field measurements. These parameterse can then be used to generate synthetic permeability fields. In the second case studied, in addition to the longitudinal dispersion coefficient specified in Section 4.1, we define the transverse dispersion coefficient as $D_T = \alpha_T |\mathbf{v}|$ where the transverse dispersivity is set

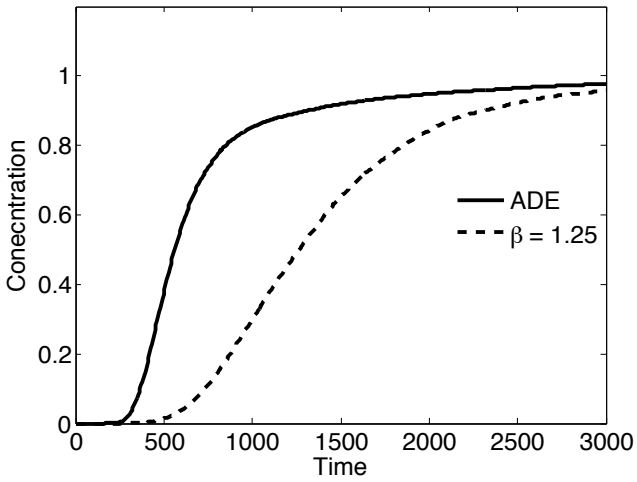

Figure 5: Comparison of the ADE and CTRW methods for flow through heterogeneous medium. Breakthrough curves of concentration $c(x_1, t)$ at $x_1 = 15.2$ km for continuous injection at the inlet $x_1 = 0$.

to $\alpha_T = 50$ m. We specify a pulse boundary condition at the inlet, injecting 10^4 particles uniformly over a 100 m distance at the top edge, $x_1 = 0$, $x_2 = L_2$.

The medium's permeability $k(\mathbf{x})$—the top subfigure in Figure 6—was constructed using a multiresolution random field generator based on the Karhunen-Loéve decomposition [51]. It represents a realization of the statistically homogeneous random field that has the mean $\overline{k} = 10^{-12}\,\mathrm{m}^2$, transformed variance $\sigma^2_{\ln k} = 1$, and anisotropic exponential covariance function with correlation lengths 200 m, 200 m, and 100 m in the x_1, x_2 and x_3 directions, respectively. Tracer was injected for the first 1000 y of the simulation.

The medium's heterogeneity causes spatial variability of the fluid velocity $\mathbf{v}(\mathbf{x})$. It is computed by rescaling the Darcy flux $\mathbf{q}(\mathbf{x})$ with the medium's (constant) porosity ω, i.e., $\mathbf{v} = \mathbf{q}/\omega$. The Darcy flux is obtained as a solution of the steady-state flow equation,

$$\mathbf{q} = -\frac{kg}{\nu}\nabla h, \qquad \nabla \cdot \mathbf{q} = 0, \tag{20}$$

where ν is the fluid's kinematic viscosity, g is the gravitational constant and $h(\mathbf{x})$ is the hydraulic head. The flow is driven by the hydraulic head gradient resulting from boundary conditions $h(x_1 = 0, x_2, x_3) = H_1$ and

$h(x_1 = L_1, x_2, x_3) = H_2$. The boundary conditions and domain discretization for this example was the same as the previous heterogeneous medium example.

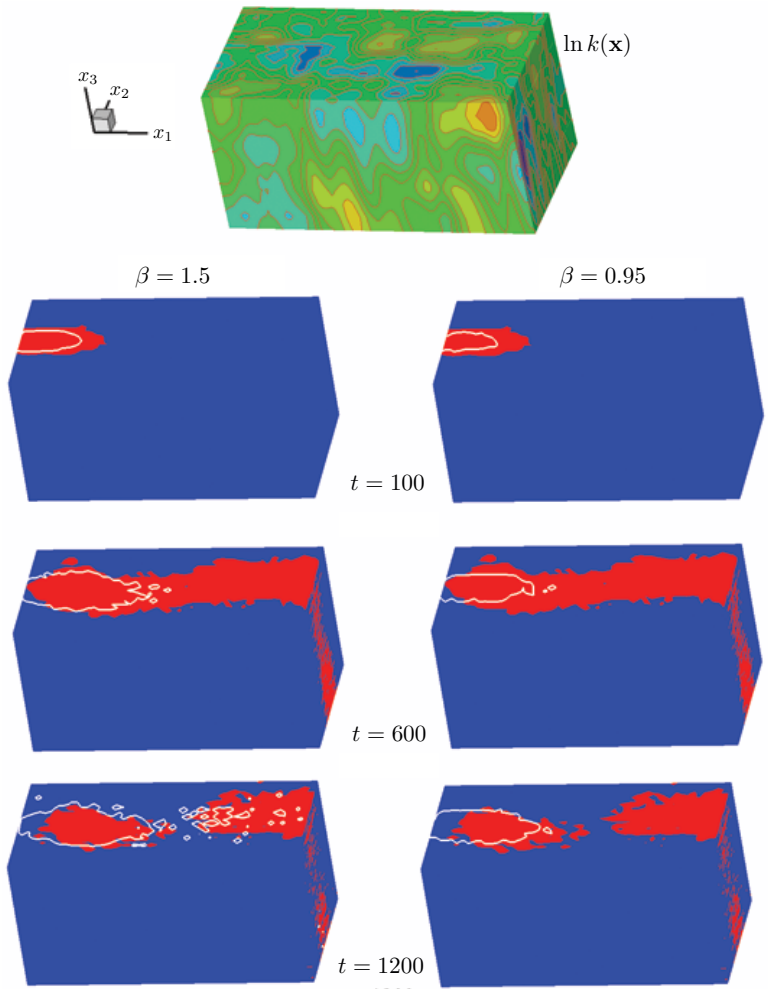

Figure 6: Comparison of the ADE and CTRW methods for flow through heterogeneous permeability field. The ADE plume is shown in red and the CTRW plume in white.

The results of these simulations are presented in Figure 6 for anomalous transport with $\beta = 1.5$ and $\beta = 0.95$, as well as for the ADE model of transport. Iso-surface plots of the model domain are shown at various times, 100 y, 600 y and 1200 y. A normalized concentration of 0.0025 was chosen for the isoline with the ADE plume shown in red and the CBPT-CTRW shown

in white. Since the tracer is injected near the top surface of the domain, the majority of the plumes travel along the top surface of the model domain. As time progresses, the plumes appear to break apart into "islands" at the top surface. The islands are due to the fact that there are low permeability zones that cause the plume to leave the top surface later reappears due to high permeability pathways. The CBPT-CTRW algorithm predicts significant attenuation of the plume for both values of β. It resulted in lower peak concentration and longer tail breakthrough curves than those resulting from the ADE. Lower values of β lead to higher values of the inlet concentration at later times, since they correspond to larger residence times in a cell. The distance traveled by the plume also decreases as β decreases. Relative to its counterpart predicted with the ADE, it spreads farther in the transverse direction.

5. Conclusions

Advection-dispersion equations (ADEs) are routinely used to describe transport phenomena in heterogeneous environments. Yet they often fail to capture subgrid heterogeneities that lead to the so-called anomalous or non-Fickian transport behavior, whose manifestations are early or late arrival times, long tails of concentration profiles, etc.

We presented a particle-based approach for modeling non-Fickian (anomalous) transport in heterogeneous environments. The approach treats a particle trajectory as a subordinated stochastic process that is described by a set of Langevin equations, which represent a CTRW at its basic level. To increase the computational efficiency and accuracy of these simulations, we employ the convolution-based particle tracking (CBPT) method.

Our analysis leads to the following major conclusions.

1. The Langevin formulation used in the CTRW-CBPT algorithm is general in that no statistical restrictions are imposed on the stochastic processes representing the spatial and temporal random increments. They can be correlated in space and time, stationary or non-stationary, their distributions are arbitrary.
2. For stationary and uncorrelated random increments, the well-known partial differential equation (PDE) formulations of CTRW in terms of generalized Fokker-Planck equations can be obtained by a generalized Kramers-Moyal expansion.

3. The CTRW-CBPT algorithm reproduces analytical solutions for both classical (ADE-based) and anomalous (a PDE formulation of CTRW) transport models, with CBPT providing a significant computational speed-up.
4. Finally, the CTRW-CBPT approach enables one to convert any existing particle-tracking code into a simulator capable of handling non-Fickian (anomalous) transport in large field-scale problems that exhibit complex parameter structures (e.g., realistic geological settings) and complex flow fields.

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