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Monte Carlo study of conservative transport in heterogeneous dual-porosity media

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Abstract

In this study, a Monte Carlo simulation method is applied to study groundwater flow and solute transport in heterogeneous, dual-porosity media. Both the hydraulic conductivity and the interregional mass diffusion rate are assumed to be spatial random variables, and their random distributions are generated through a Fast Fourier Transform (FFT) technique. A block-centered finite difference (FD) method is used to solve the flow equation. Based on the generated flow fields, a random walk particle-tracking algorithm is invoked to study the solute transport. The mass diffusion between the mobile and immobile water regions is simulated by a two-state, homogeneous, continuous-time Markov chain. The Monte Carlo simulation results are compared to those obtained through the first-order, Eulerian perturbation method. It is shown from the comparison that the first-order analytical method is robust for predicting mean concentration in mild heterogeneous dual-porosity media. However, large deviations are observed between the analytical and Monte Carlo results for predicting transport in moderately-highly heterogeneous media. The Monte Carlo method is also used to study the variance of the solute flux through a control plane.

Keywords: Monte Carlo simulation method; Hydraulic conductivity; Markov chain

1. Introduction

The dual- or double-porosity model was initially introduced to simulate groundwater flow (Barenblatt et al., 1960; Warren and Root, 1963; Duguid and Lee, 1977; Moench, 1984) and solute transport (Coats and Smith, 1964; van Genuchten and Wierenga, 1976; Bibby, 1981; Gerke and van Genuchten, 1993a,b) in fissured or fractured media. This model assumes that a fractured medium can be described by two completely overlapping continua, one representing the fracture networks and the other representing the porous matrix. The groundwater flow or/and solute transport is described by two equations coupled together with a term that characterizes the exchange of water or solutes between the two continua. This model was later used to describe the preferential movement of water and solutes at the field scale, a phenomenon that is widely believed to occur in most natural media in

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the subsurface (e.g. van Genuchten et al., 1990; Gish and Shirmohammadi, 1991). The preferential flow results in a rapid movement of solutes along those preferential pathways and a heavy tail for the solute mass flux breakthrough curve due to the kinetic mass transfer between the mobile and immobile water regions.

More recently, the dual-porosity concept has been extended to the so-called multi-rate models that involve a series of rate-limited mass transfer equations to account for continuous pore size distribution of the media (e.g. Villermaux, 1981; Pedit and Miller, 1994, 1995; Chen and Wagnet, 1995; Haggerty and Gorelick, 1995) and distribution functions are typically used to describe the distribution of the interregional mass diffusion coefficients. The conductivity heterogeneity, however, was usually not considered in these models.

It has been widely recognized that media heterogeneities, such as the spatial variation of hydraulic conductivity, have significant influence on groundwater flow and solute transport. Owing to the limited available data to deterministically describe the media's heterogeneities, stochastic method has been popularly used to address flow and transport in these media, and significant progress has been made both theoretically and experimentally over the last three decades (e.g. Dagan, 1989; Gelhar, 1993; Cushman, 1997). However, most of these studies focused on the flow and transport in the one-domain (unstructured) porous medium. Recently, some stochastic studies were conducted to study solute transport in dual-porosity media by coupling the interregional mass diffusion process with the dispersion process (Harvey and Gorelick, 1995; Haggerty and Gorelick, 1995, 1998; Li and Brusseau, 2000). Huang and Hu (2000) applied Eulerian perturbation method to set up the theory for conservative transport in heterogeneous dual-porosity media. Painter et al. (2001) used a similar mobile/immobile model, coupled with equilibrium sorption in both mobile and immobile regions, to address the effect of spatial variability in a stochastic Lagrangian framework. Huang and Hu (2001) later extended their model of conservative tracer transport in dual-porosity media to reactive transport by incorporating the kinetic sorption into both mobile and immobile regions. In their study, the hydraulic conductivity, mass transfer rate coefficient and the sorption distribution coefficients were all assumed to be spatial random variables and a first-order analytical solution for the mean concentration was obtained in transform space. It is shown by Huang and Hu (2000) that interregional mass diffusion will significantly increase plume dispersion in both longitudinal and transverse directions, and will make the plume more negatively skewed and give the breakthrough curve a long tail. Furthermore, randomness of the interregional mass diffusion coefficient will increase the plume dispersion and make the plume more skewed.

The analytical approach provides a simple and clear mathematical expression for the role of the heterogeneous mass transfer process on solute transport. The application of this approach to real field solute transport, however, is limited by some simplification assumptions used in the theory development, such as constant mean velocity, small variances of the log-conductivity and rate coefficient, weakly stationary conductivity field, and infinite domain without any source/sink. Numerical Monte Carlo simulation is another commonly applied stochastic approach to flow and solute transport in heterogeneous media. This approach is computationally demanding, but flexible to complex boundary geometry and with no limitation to the medium heterogeneity. The analytical and Monte Carlo methods have been complementary to each other in the stochastic theory development of flow and transport in the one-domain field (e.g. Bellin et al., 1992; Tompson 1993; Hassan et al., 1997, 1998). In this study, an efficient Monte Carlo simulation algorithm is developed to simulate the transport of conservative transport in a dual-porosity medium. The purpose of this study is to evaluate the accuracy and validity of the analytical solution developed by Huang and Hu (2000) and to study the variance about the mean prediction. The variance calculation was beyond the scope of Huang and Hu (2000) study. In Section 2, the analytical solution by Huang and Hu (2000) is outlined. Section 3 presents a Monte Carlo numerical simulation algorithm for groundwater flow and conservative transport in a heterogeneous dual-porosity medium. In Section 4, analytical results are compared with those obtained from Monte Carlo simulations to evaluate the accuracy of the analytical solution. Monte Carlo method is further applied to investigate the uncertainty

about the mean prediction. The main conclusions of this study are given in Section 5.

2. First-order analytical solution

For conservative solute transport in a dual-porosity medium, the concentration in mobile water, C_m, satisfies, on the local scale, the following equation (Huang and Hu, 2000)

$$\theta_m \frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_m d_{ij} \frac{\partial C_m}{\partial x_j}\right) - \frac{\partial (q_i^* C_m)}{\partial x_i} - a(C_m - C_n) \quad (1)$$

where θ_m is the fractional water content in the mobile region, q_i^* is the specific discharge, and d_{ij} is the local dispersion coefficient tensor, a is the interregional mass diffusion coefficient, and C_n is the solute concentration in the immobile water region. The repeated indices indicate Einstein summation. The concentrations in the mobile and immobile water regions are related by a first-order transfer equation to account for the rate-limited, mass diffusion process between the two regions,

$$\theta_n \frac{\partial C_n}{\partial t} = a(C_m - C_n) \quad (2)$$

where θ_n is the fractional water content in immobile water. In Huang and Hu (2000), the mean specific discharge is assumed to be constant and in the x_1 direction so that $\bar{q}_1^* = q$, $\bar{q}_2^* = \bar{q}_3^* = 0$, where the overbar represents the mean or ensemble, and the local dispersion coefficient tensor is constant and diagonal with $d_{ii} = d_i$ $(i = 1, 2, 3)$. Note that Eq. (2) is mathematically similar to a kinetic chemical sorption model, but the cause of this nonequilibrium behavior described by Eq. (2) is rate limitations in the diffusive mass transfer between the mobile and immobile water. The mass transfer rate a is defined as $a = (\beta/\chi^2)D_a$, where β is a factor depending on the geometry of the aggregates, χ represents the characteristic distance (L) from the center of a fictitious matrix block to the fracture boundary, and D_a is the effective ionic or molecular diffusion coefficient (L^2T^{-1}) of the matrix block near the interface. In this study, we will not study the parameters, β, χ and D_a, individually, but the factor of their combination, a.

It was assumed that the log-conductivity in the mobile region, $ln\ K$, and a are spatial random variables (Huang and Hu, 2000), which account for the spatial variations of conductivity and mass transfer process, respectively. The randomness of the parameters, in turn, results in the random velocity field in mobile water and concentrations in both regions. In the usual fashion, these random variables are decomposed into their means and perturbation parts, and substituted into Eqs. (1) and (2). Eqs. (1) and (2) become stochastic governing equations, from which one can seek the solutions for the means of the concentrations and variances about the means. Huang and Hu (2000) provided a first-order solution for mean solute concentration in mobile water. Its expression in spatial-Fourier and temporal-Laplace transforms is given as

$$\tilde{\hat{C}}_m(\mathbf{k},\omega) = \tilde{\hat{F}}^{-1}(\mathbf{k},\omega)\Bigg\{\theta_m \hat{C}_m^0 + \Bigg[\bar{a} - \frac{ik_j}{(2\pi)^3}\tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{q}_j} - \frac{1}{(2\pi)^3}\tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{\alpha}} + \frac{\tilde{W}\bar{\alpha}}{(2\pi)^3}\tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{\alpha}} - \tilde{W}\overline{\alpha\alpha}(0)\Bigg]\tilde{\hat{I}}_1^{-1}\theta_n \hat{C}_n^0\Bigg\} \quad (3)$$

where ^ and ~ represent spatial-Fourier and temporal-Laplace transforms, respectively, $\mathbf{k}$ and ω are wave number and Laplace transformed time; $*$ represents the convolution operator and the subscript, $\mathbf{k}$, indicates the variable on which the convolution operates. α is the perturbation term of a. C_m^0 and C_n^0 are the initial concentrations in the mobile and immobile water, respectively, and

$$\tilde{\hat{F}}(\mathbf{k},\omega) = \theta_m\omega + \theta_m d_i k_i^2 + iqk_1 + \bar{a} - \bar{a}\tilde{\hat{I}}_1^{-1}\tilde{\hat{I}}_2 - \tilde{W}\overline{\alpha\alpha}(0) + \tilde{W}\overline{\alpha\alpha}(0)\tilde{\hat{I}}_1^{-1}\tilde{\hat{I}}_2 - \frac{ik_j}{(2\pi)^3} \times (ik_i\tilde{\hat{B}} *_{\mathbf{k}} \overline{\hat{q}_i\hat{q}_j} + \tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{q}_j} - \tilde{\hat{I}}_1^{-1}\tilde{\hat{I}}_2\tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{q}_j}) - \frac{1-\tilde{W}\bar{a}}{(2\pi)^3}(ik_i\tilde{\hat{B}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{q}_j} + \tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{\alpha}} - \tilde{\hat{I}}_1^{-1}\tilde{\hat{I}}_2\tilde{\hat{G}} *_{\mathbf{k}} \overline{\hat{\alpha}\hat{\alpha}}) \quad (4a)$$

$$\tilde{\hat{B}}^{-1}(\mathbf{k},\omega) = \theta_m\omega + \theta_m d_i k_i^2 + iqk_1 + \bar{a} - \frac{\bar{a}^2}{\theta_n\omega + \bar{a}} \quad (4b)$$

$$\tilde{\hat{G}}(\mathbf{k},\omega)=\tilde{\hat{B}}(\mathbf{k},\omega)\left[1-\frac{\bar{a}}{\theta_n\omega+\bar{a}}\right] \tag{4c}$$

$$\tilde{W}(\omega)=1/(\theta_n\omega+\bar{a}) \tag{4d}$$

$$\tilde{\hat{I}}_1(\mathbf{k},\omega)=\theta_n\omega+\bar{a}-\tilde{W}\overline{\alpha\alpha}(0)-\frac{1-\tilde{W}\bar{a}}{(2\pi)^3}\tilde{\hat{G}}*_{\mathbf{k}}\overline{\hat{\alpha}\hat{\alpha}} \tag{4e}$$

$$\tilde{\hat{I}}_2(\mathbf{k},\omega)=\bar{a}-\tilde{W}\overline{\alpha\alpha}(0)-\frac{1-\tilde{W}\bar{a}}{(2\pi)^3}[ik_i\tilde{\hat{B}}*_{\mathbf{k}}\overline{\hat{\alpha}\hat{q}_i}+\tilde{\hat{G}}*_{\mathbf{k}}\overline{\hat{\alpha}\hat{\alpha}}] \tag{4f}$$

Eq. (3) is the first-order solution of mean concentration in transform space for a conservative solute in a heterogeneous dual-porosity medium. It is shown from Eq. (3) that $\bar{C}_m$ is explicitly expressed by various coefficients and correlation functions, and can be calculated through the Fast Fourier Transform (FFT) method (Deng et al., 1993).

It is shown from Eqs. (3) and (4a)–(4f) that various factors, including the mean values of the various parameters and their correlation functions, and initial concentrations in the mobile and immobile water, will affect the plume spreading. Huang and Hu (2000) studied the effects of these factors on mean concentration as well as the spatial moments. The various spatial moments are related to the mean concentration through the following equations,

$$M=\int_{R^2}\theta_m\bar{C}_m\mathrm{d}\mathbf{x} \tag{5a}$$

$$X_1^i=1/M\int_{R^2}\theta_m x_i\bar{C}_m\mathrm{d}\mathbf{x} \tag{5b}$$

$$X_2^i=1/M\int_{R^2}\theta_m x_i^2\bar{C}_m\mathrm{d}\mathbf{x}-(X_1^i)^2 \tag{5c}$$

where M is the 0th moment, X_1^i and X_2^i are the first and second moments, respectively, in the x_i direction. Physically, the 0th moment is the solute total mass, the first moment is the plume mean movement, and the second moment represents the plume spreading.

Huang and Hu (2000) found that the spatial variations of rate coefficient a significantly enhance the longitudinal spreading of the plume and make the plume distribution more skewed. Their findings reveal the necessity to account for the spatial variability of the mass transfer process to predict the transport in dual-porosity media. However, their solution is of first-order accuracy in terms of the log-conductivity variance, σ_f^2. So the solution is only applicable to mild heterogeneous media. In Section 3, a Monte Carlo simulation algorithm, involving the random walk particle-tracking technique, will be developed to simulate the solute transport and mass transfer process in dual-porosity media.

3. Monte Carlo numerical simulation

In this section, a Monte Carlo numerical simulation algorithm is developed to simulate the conservative transport in dual-porosity media. The objectives of the numerical study are to verify the analytical solution for the mean concentration and to estimate the uncertainties about the mean predictions, which are beyond the scope of the analytical study because of the mathematical complexity involved. The simulation algorithm consists of the following five steps:

1. Generating realizations of the random hydraulic conductivity fields and the mass transfer rate fields with specified correlation functions,
2. Solving the flow equations to obtain the velocity field for each realization of the hydraulic conductivity distribution,
3. Employing particle-tracking simulations within an inner portion of the domain that is not affected by the boundaries to solve the transport problem coupled with rate-limited mass transfer process for each realization,
4. Repeating steps 1–3, and
5. Ensemble averaging over all realizations to obtain the mean and variance of the concentration distribution. The averaged mean concentration will be compared with the analytical solution.

3.1. Generating random hydraulic conductivity fields

The first step of the Monte Carlo numerical simulation method is to generate independent and equally probable realizations of the hydraulic conductivity and interregional mass diffusion coefficient fields. Several methods are available for this purpose (e.g. Clifton and Neuman, 1982; Smith and Freeze, 1979; Tompson et al., 1989; Gutjahr, 1989). Among them, the method based on FFT is chosen in this study owing to its computational efficiency when

the correlation function is given. The basic concept of this method is to generate a set of uniformly distributed random numbers (white noise) by using a random number generator. By taking the FFT of these numbers, the resulting spectrum will have a uniform density of unity. If we multiply the transformed numbers by the square root of the spectral density function of the conductivity field (the Fourier transform of *ln K* covariance), the resulting numbers will have the same spectrum as that of the hydraulic conductivity field. Finally taking the inverse FFT of those numbers gives a set of numbers in real space having the same correlation structure as that of the conductivity field.

3.2. Solving flow problem for each hydraulic conductivity realization

The realizations of the hydraulic conductivity field coupled with appropriate boundary conditions are used to solve the flow equation to obtain the potential field and subsequently the velocity field. A five-point block-centered finite difference (FD) scheme is employed to discretize the steady-state flow equation. The linear system resulting from the FD discretization of the flow equation is solved via an iterative bi-conjugate gradient method (e.g. Press et al., 1992). Darcy's law is then applied to obtain the velocity field for the entire domain. The mean uniform velocity in the x_1 direction is obtained by specifying head values along the left and right boundaries and by assuming the other two boundaries to be impervious. Tests on the accuracy of the flow solver and the stationarity of the obtained velocity field are described in detail in Hassan et al. (1998).

3.3. Particle tracking for solving the transport equation coupled with rate-limited mass transfer

This part uses the particle-tracking technique to solve the transport equation (e.g. Freeze, 1975; Smith and Freeze, 1979; Smith and Schwartz, 1980, 1981; Rubin, 1990; Bellin et al., 1992; Tompson 1993; Hassan et al., 1997). The solution of the transport equation is approximated by tracking the particles' movements in time and space. The random walk method is one of the most common particle-tracking methods. The spatial locations of all particles are updated according to the equation (Tompson and Gelhar, 1990)

$$\mathbf{X}_{t+\Delta t} = \mathbf{X}_t + [\mathbf{V}(\mathbf{X}_t, t) + \nabla\cdot\mathbf{d}(\mathbf{V}(\mathbf{X}_t, t))]\Delta t + [2\mathbf{d}(\mathbf{V}(\mathbf{X}_t, t)\Delta t]^{1/2}\cdot\mathbf{Z} \quad (6)$$

where $\mathbf{Z}$ is a vector of random numbers drawn from a normal distribution with zero mean and unit variance; $\mathbf{V}(\mathbf{X}_t, t)$ is the velocity vector of the mobile water and $\mathbf{d}$ is the local dispersion coefficient tensor. The second term on the right-hand side moves the particles advectively on the basis of the local velocity. The third term is important when stagnation regions exist within the flow field. The last term accounts for the local-scale dispersion.

The above random walk method is applied to solve the transport equation for the concentration over each realized conductivity field. At any time, the concentration distribution is obtained by superimposing a fine grid on the computation domain. The concentration within each cell is obtained by counting the total number of particles within each cell. In addition, the solute flux across a downstream control plane is also calculated by counting the number of particles crossing the plane within each time interval.

The key issue associated with the random walk method here is how to properly simulate the mass transfer process between the mobile and immobile water within the frame of particle-tracking methods. Valocchi and Quinodoz (1989) provided a detailed discussion on the random walk method for simulating the transport of kinetically sorbing solutes. However, they assumed a one-dimensional flow field and deterministic reaction rate coefficient. Hassan et al. (1997) extended the reactive particle-tracking simulation to a two-dimensional heterogeneous flow field with spatially variable reaction rate coefficient. A two-state Markov chain model governed by a transitional probability matrix, which is related to the reaction rates, simulates the kinetic sorption process in their study. In our study, we extend Hassan et al's. (1997) random walk method to the case of nonreactive transport in heterogeneous medium with random mass transfer between the mobile and immobile water.

Consider a sequence of phase changes experienced by a single particle between two states (or phases): the mobile water (state *m*) and immobile water (state *n*). At any instant of time the particle can exist only in

either one of these two states. For convenience, let's rewrite the governing Eqs. (1) and (2) in the following equivalent forms

$$\frac{\partial C_m}{\partial t} + \frac{\partial C_n^*}{\partial t} = \frac{\partial}{\partial x_i}\left(d_{ij}\frac{\partial C_m}{\partial x_j}\right) - \frac{\partial (V_i C_m)}{\partial x_i} \tag{7}$$

and

$$\frac{\partial C_n^*}{\partial t} = \frac{a}{\theta_m} C_m - \frac{a}{\theta_n} C_n^* \tag{8}$$

where $C_n^* = (\theta_n/\theta_m)C_n$ represents the solute mass transferred into the immobile water per unit volume of the mobile water.

Parzen (1962) showed that the stochastic analogue of Eq. (8) is a homogeneous, continuous-time, two-state Markov chain denoted as $\{Y(t), t > 0\}$ with state space $\{m, n\}$, where m and n indicate that the particle is in the mobile and immobile water, respectively. The rates at which a particle leaves states m and n are a/θ_m and a/θ_n, respectively. The Markov chain is completely characterized if its transitional probabilities are known. The transitional probabilities measure the probability of transition between any combinations of the two states (m–m, m–n, n–m, n–n), and are obtained by solving a system of differential equations written as

$$\frac{\mathrm{d}p_{m,m}(t)}{\mathrm{d}t} = -\frac{a}{\theta_m}p_{m,m}(t) + \frac{a}{\theta_n}p_{m,n}(t) \tag{9a}$$

$$\frac{\mathrm{d}p_{m,n}(t)}{\mathrm{d}t} = -\frac{a}{\theta_n}p_{m,n}(t) + \frac{a}{\theta_m}p_{m,m}(t) \tag{9b}$$

$$\frac{\mathrm{d}p_{n,n}(t)}{\mathrm{d}t} = -\frac{a}{\theta_n}p_{n,n}(t) + \frac{a}{\theta_m}p_{n,m}(t) \tag{9c}$$

$$\frac{\mathrm{d}p_{n,m}(t)}{\mathrm{d}t} = -\frac{a}{\theta_m}p_{n,m}(t) + \frac{a}{\theta_n}p_{n,n}(t) \tag{9d}$$

where the subscripts of p represent the initial and final states associated with the transition. The solution of the above system of equations is given by

$$\begin{bmatrix} p_{m,m}, & p_{m,n} \\ p_{n,m}, & p_{n,n} \end{bmatrix} = \begin{bmatrix} 1-\frac{\theta_n}{\theta_m+\theta_n}[1-\mathrm{e}^{-(a/\theta_m+a/\theta_n)\Delta t}], & \frac{\theta_n}{\theta_m+\theta_n}[1-\mathrm{e}^{-(a/\theta_m+a/\theta_n)\Delta t}] \\ \frac{\theta_m}{\theta_m+\theta_n}[1-\mathrm{e}^{-(a/\theta_m+a/\theta_n)\Delta t}], & 1-\frac{\theta_m}{\theta_m+\theta_n}[1-\mathrm{e}^{-(a/\theta_m+a/\theta_n)\Delta t}] \end{bmatrix} \tag{10}$$

In summary, particles in the mobile water are transported in each time interval according to Eq. (6). At the end of each time interval, a uniform [0, 1] random number, X, is drawn for each particle in the mobile water and is compared to $p_{m,n}$. It should be noted that $p_{m,n}$ is different for each particle because of the spatial variability of the mass transfer coefficient, a. The final state of the particles in the mobile water is adjusted according to

$$Y(t+\Delta t) = \begin{cases} m & \text{if } X > p_{m,n} \\ n & \text{if } X \le p_{m,n} \end{cases} \tag{11a}$$

For the particles in the immobile water, the spatial position will not change within that time interval. The final state of each particle in the immobile water is adjusted in a similar way as

$$Y(t+\Delta t) = \begin{cases} n & \text{if } X > p_{n,m} \\ m & \text{if } X \le p_{n,m} \end{cases} \tag{11b}$$

At the beginning of the next time step, only particles in the mobile water are allowed to move with the underlying velocity field. Particles in the immobile zones are fixed in space for the entire time step and their final status will be adjusted at the end of the time step according to Eq. (11b).

This process is repeated at each time interval during the entire simulation period. In the next section, the numerical results will be compared with the analytical solution (Eq. (3)).

4. Numerical results and discussion

4.1. Problem setup

The synthetic domain is set to be rectangular with a size of 53 × 25.6 (as shown in Fig. 1) (normalized by the hydraulic conductivity correlation length λ). The left and right boundaries are set to be constant head boundaries while the top and bottom boundaries are set to be no flow boundaries. The mean hydraulic gradient **J** is fixed at 0.05 and aligned with the horizontal coordinate. The geometric means of hydraulic conductivity ($\bar{K}_g$) and mass transfer rate coefficient ($\bar{a}_g$) are chosen to be 1.0 m/d and 0.002 d^{-1}, respectively. Other parameters include $\theta_m = 0.25$, $\theta_n = 0.1$, $\alpha_L = 0.5$ m and $\alpha_T = 0.05$ m. To avoid the boundary effects (e.g. Bellin et al., 1992), the initial plume center is located 10 correlation lengths away from the left

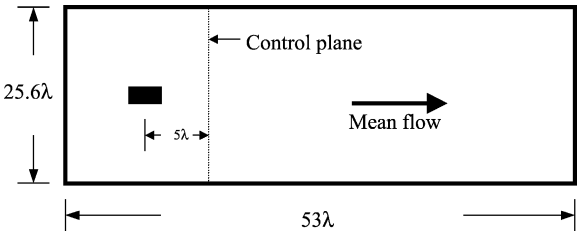

Fig. 1. Configuration of the computation domain.

boundary and the initial plume is chosen to be a rectangle with a size of $3\lambda \times 1\lambda$. The entire domain is discretized with a 256×128 grid, which yields five cells per correlation length. A control plane located five correlation lengths away downstream from the initial plume center is set to sample the solute flux. The time step for particle tracking is chosen to be 0.05 d. To verify the accuracy and validity of the first-order analytical solution, we choose two values of $\ln K$ variance σ_f^2, 0.4 and 1.2, to represent mild and moderately heterogeneous media, respectively. In our study, the covariance function of the hydraulic conductivity field is chosen to be isotropic Gaussian as

$$\overline{ff}(\mathbf{z}) = \sigma_f^2 \exp[-(z_1^2/\lambda^2 + z_2^2/\lambda^2)] \tag{12}$$

where f is the log-conductivity perturbation and $\mathbf{z}$ is the lag space vector. It is notable that both the analytical solution and FFT-based random field generator do not require the $\ln K$ covariance to be Gaussian. The covariance function can take other forms as well. Fig. 2 shows the comparison between the theoretical covariance function and numerically generated covariance function averaged over 2000 conductivity realizations. The statistics of the generated conductivity fields match the theoretical curve very well. Huang and Hu (2000) investigated the roles of the cross correlation structure between $\ln K$ and a. In this study, following their approach, we assume a and $\ln K$ are perfectly negatively correlated, and a is obtained through

$$a(\mathbf{x}) = \bar{\alpha}_g e^{-f(\mathbf{X})} \tag{13}$$

4.2. Monte Carlo simulation results and comparison with analytical solution

A set of 2000 independent and equally probable hydraulic conductivity fields is generated first. For each realization of the conductivity field, we solve the flow equation to obtain the velocity field, and then apply the particle-tracking technique introduced in Section 3 to solve the transport equation and obtain the concentration distribution and solute flux for each realization. The numerical mean concentration and solute flux are obtained by averaging over all 2000 realizations. Eqs. (5a)–(5c) is then used to calculate the spatial moments (the first and second moments) of the ensemble averaged mean concentration. The numerical mean and spatial moments are compared to Huang and Hu's (2000) analytical results.

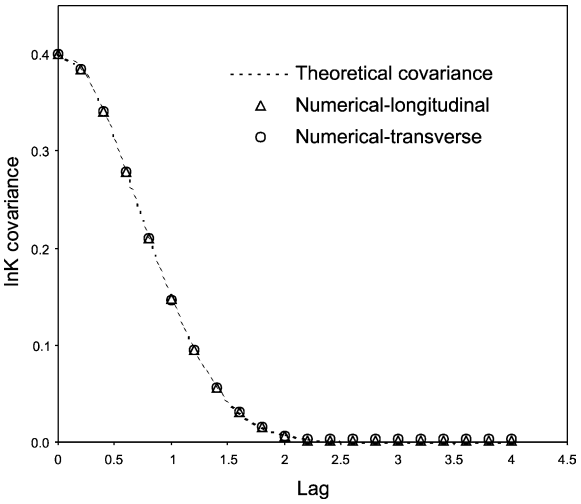

Fig. 2. Comparison of the theoretical and the FFT-based numerical covariance functions.

Fig. 3 shows the comparison of spatial moments obtained from Monte Carlo simulation and Huang and Hu's (2000) analytical results for two cases: $\sigma_f^2 = 0.4$ and $\sigma_f^2 = 1.2$. The first and second spatial moments measure how fast the plume center moves and how wide the mean plume spreads from its center along both the longitudinal and transverse directions. Fig. 3(a) shows the comparison of the first moment X_1. First of all, for the case of $\sigma_f^2 = 0.4$, representing mild heterogeneous media, the Monte Carlo simulation result matches the analytical result very well. The difference on the first moment X_1 is almost undetectable all the way through the entire calculation time. However, in the case of $\sigma_f^2 = 1.2$, representing moderately heterogeneous media, though the two approaches match very well at early travel time,

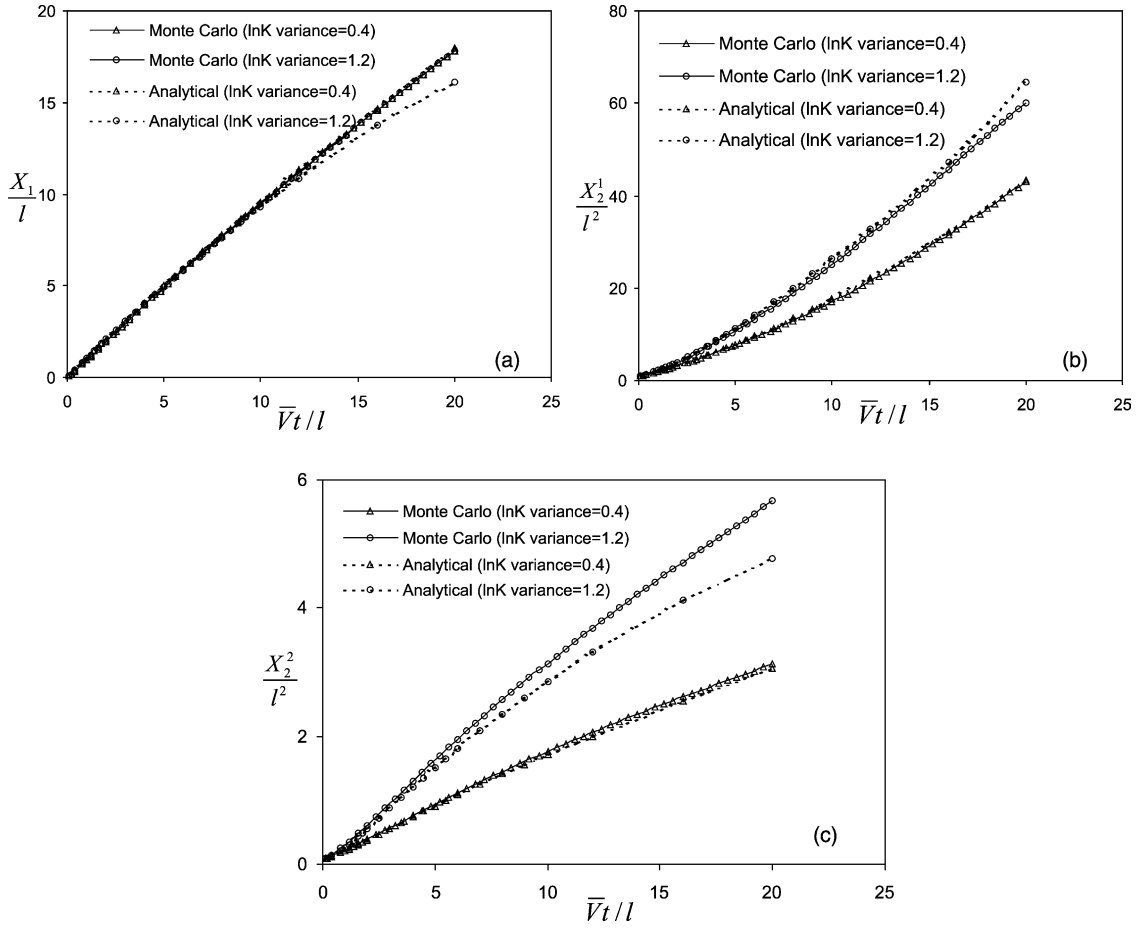

Fig. 3. Comparison of spatial moments for the cases of $\sigma_f^2 = 0.4$ and $\sigma_f^2 = 1.2$: (a) first moment; (b) second longitudinal moment; (c) second transverse moment.

the analytical approach predicts lower first moment at large travel time than the Monte Carlo simulation does. In both cases, the Monte Carlo approach predicts almost the same first moment, which is expected since the only difference between two cases is the variance of ln K, all other parameters being the same. The reason for this large time deviation is not clear, but might be attributed to the accuracy of the analytical solution (Bellin et al., 1992; Hu et al., 1999, 2002)). This issue will be addressed in more details later in this section. Fig. 3(b) and (c) exhibit the comparisons of the second moments, longitudinal X_2^1 and transverse X_2^2, between the two approaches. For the case of $\sigma_f^2 = 0.4$, the two approaches match very well and the differences on the second longitudinal and transverse moments are negligible. The agreement demonstrates the accuracy of the analytical solution for estimating the plume spreading in mild heterogeneous media. In addition, the agreement also verifies the validity of the random walk particle-tracking approach we developed in Section 3. The Markov chain governed by Eq. (10) is quite robust for simulating the mass transfer process between the mobile and immobile water. However, for the large ln K variance case, $\sigma_f^2 = 1.2$, the analytical approach overestimates the second longitudinal moment and underestimates the second transverse moment. The deviations from the Monte Carlo results become more pronounced at the large travel time. The solution of Huang and Hu (2000) is of first-order accuracy in terms of ln K variance σ_f^2 due to truncations of the higher-order terms. Hu et al.

(1999, 2002) analyzed the effect of second-order correction of transport formulation to the spatial moments. They found that for both conservative and reactive transport, the second-order correction decreases the second longitudinal moment and increases the transverse moment, yielding closer agreement with the Monte Carlo simulation results than the first-order theory does for transport in moderately and highly heterogeneous media. Thus, the results shown in Fig. 3(b) and (c) are consistent with Hu et al. (1999, 2002) results.

In summary, for transport in mild heterogenous media, the analytical solution and Monte Carlo simulation match very well on the first and second spatial moments. Though the analytical solution provides a slightly larger second longitudinal moment and a slightly less transverse moment, the difference between the two approaches is practically negligible. Huang and Hu's (2000) analytical solution is quite accurate for predicting plume spreading in mild heterogeneous dual-porosity media. However, their solution overestimates the longitudinal spreading and underestimates the transverse spreading for transport in moderately and highly heterogeneous dual-porosity media. Caution is needed when applying the analytical solution if σ_f^2 is above 1.0.

Fig. 4(a)–(c) show the comparison of mean plumes at early, intermediate and large travel times obtained from the analytical and Monte Carlo approaches for the case of $\sigma_f^2 = 0.4$. The numerical mean concentration is obtained by averaging the concentrations of all 2000 realizations. In this case, as shown in Fig. 4(a)–(c), the mean concentrations predicted by the two approaches match very well through the entire simulation period. The differences on peak values of the mean concentrations and the plume spreading patterns are practically negligible. Such good agreement on the mean concentrations is consistent with the moment results shown in Fig. 3(a)–(c) and further supports the accuracy of the analytical solution and the validity of the random walk particle-tracking algorithm developed in Section 3. However, such a good match no longer holds for the case of $\sigma_f^2 = 1.2$. Fig. 4(d)–(f) show the comparison of mean concentrations for the case of $\sigma_f^2 = 1.2$. Though the two approaches match fairly well at the early travel time, the analytical results deviate from that of the Monte Carlo simulation with the increase of travel time. At the large travel time, as shown in Fig. 4(f), the analytical solution predicts a much heavier tail than the Monte Carlo simulation does. Much more mass is accumulated onto the tail of the mean plume, retarding the bulk movement of the mean plume and enhancing the longitudinal spreading. This effect may explain the reasons why the analytical approach predicts less first moment and larger second longitudinal moment as shown in Fig. 3. In summary, the comparison of the mean plumes shown in Fig. 4 also supports the accuracy of the analytical solution for modeling transport in mild heterogeneous dual-porosity media and the validity of the particle-tracking algorithm. However, the comparison also indicates that the applicability of Huang and Hu's (2000) analytical solution for moderately and highly heterogeneous dual-porosity media is suspicious since it significantly overestimates the tailing behavior. So it is worthwhile to compare the breakthrough curves predicted by both approaches.

Fig. 5(a) and (b) depict the comparison of mean solute fluxes across a control plane predicted by the analytical and Monte Carlo approaches for two cases: $\sigma_f^2 = 0.4$ and $\sigma_f^2 = 1.2$. The numerical mean solute flux is obtained by averaging the solute fluxes of 2000 realizations. For the case of $\sigma_f^2 = 0.4$, as shown in Fig. 5(a), the two curves match very well, similar to the results shown in the previous figures. It is notable that the two tails match extremely well, as a major evidence of the validity of the Markov chain model developed in Section 3 to simulate the mass transfer between the mobile and immobile water. In addition, the peak flux values and arrival times are in good agreement as well. Fig. 5(b) shows the comparison of flux curves for the case of $\sigma_f^2 = 1.2$. The analytical solution significantly overestimates the tailing behavior of the flux curves and also underestimates the peak flux value. The results shown here are consistent with the results shown in Fig. 4(f), where the analytical approach accumulates more mass onto the tail of the mean plume than the Monte Carlo simulation.

One advantage of the Monte Carlo simulation, as we mentioned in Section 1, is that it also provides uncertainty measurements associated with the predicted means. Huang and Hu (2000) gave a closed-form solution for the mean concentration, but did not

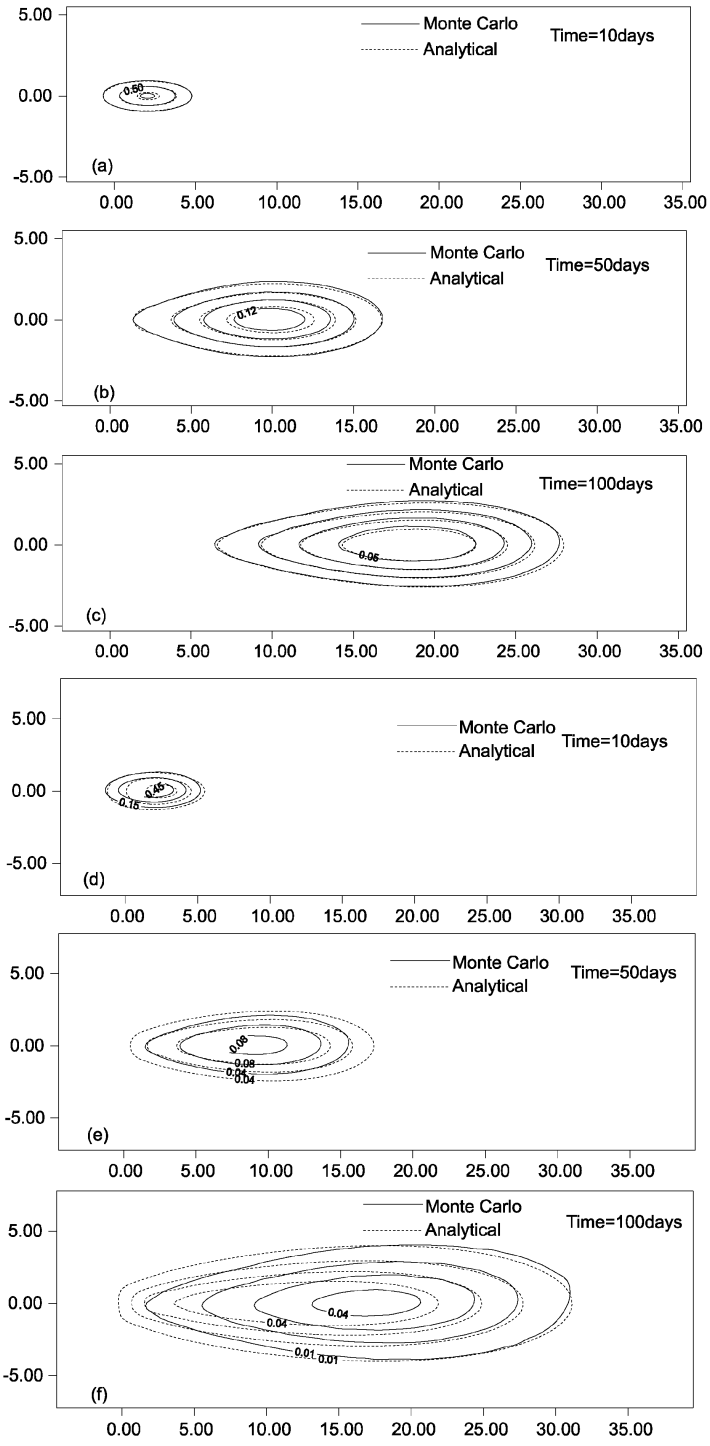

Fig. 4. Comparison of mean plume at early, intermediate and large travel times: (a)–(c) mean plume for $\sigma_f^2 = 0.4$; (d)–(f) mean plume for $\sigma_f^2 = 1.2$.

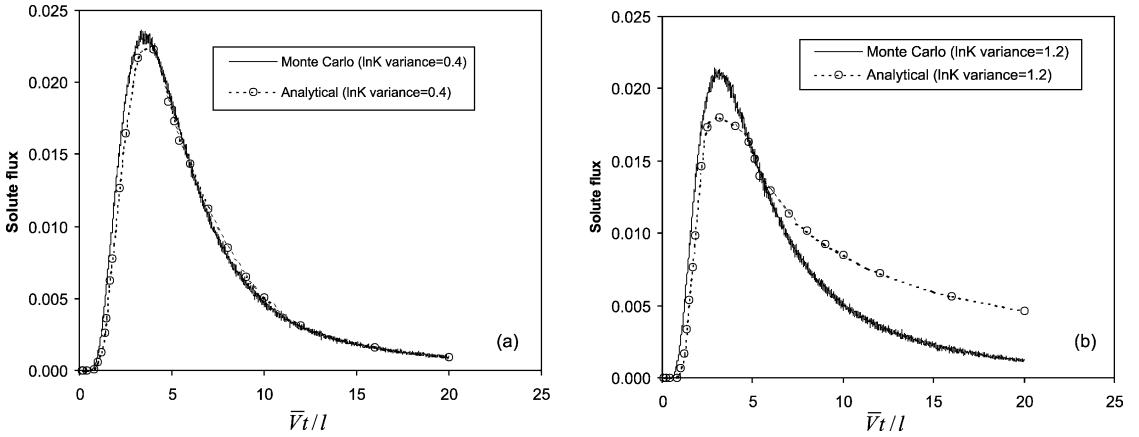

Fig. 5. Comparison of solute flux across a control plane located five correlation lengths downstream: (a) comparison for $\sigma_f^2 = 0.4$; (b) comparison for $\sigma_f^2 = 1.2$.

provide the variance of the concentration due to complexity of the mathematics. Fig. 6 shows the variance of the solute flux corresponding to the mean flux curves shown in Fig. 5(a)–(b). According to Fig. 6, as σ_f^2 increases, uncertainties on the arrival time, peak flux and tail behavior all increase due to more heterogeneity. The increase of uncertainty on peak flux is most pronounced.

5. Conclusions

In this study, a Monte Carlo simulation algorithm involving a random walk particle-tracking technique was developed to simulate the transport of conservative tracers in heterogeneous dual-porosity media, coupled with a heterogeneous mass transfer process between the mobile and immobile water.

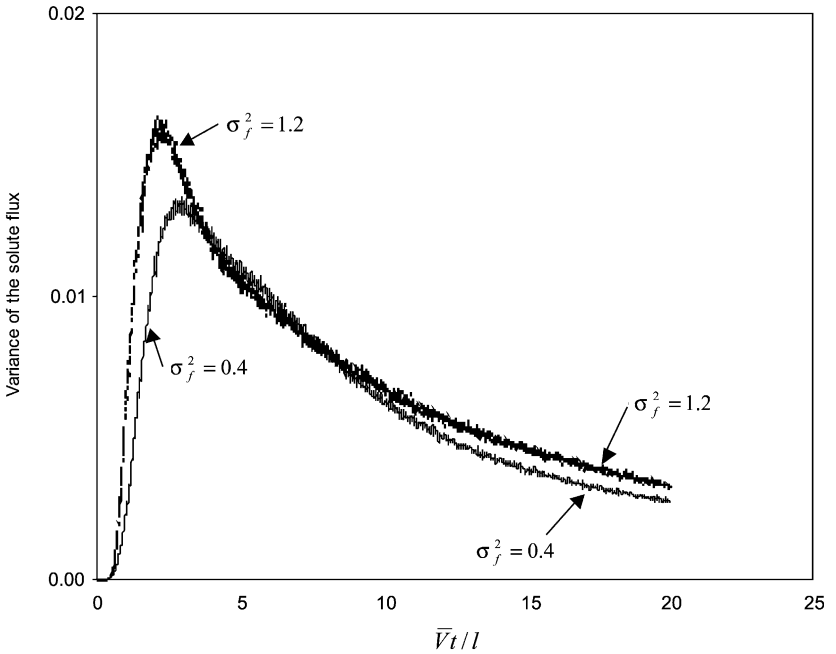

Fig. 6. Comparison of the variance of solute flux for the cases of $\sigma_f^2 = 0.4$ and $\sigma_f^2 = 1.2$.

The hydraulic conductivity and mass transfer rate coefficient were treated as spatial random variables. The Monte Carlo simulation was performed for two representative cases, $\sigma_f^2 = 0.4$ and $\sigma_f^2 = 1.2$, representing mild and moderately heterogeneous media, respectively. The simulated results were compared to the stochastic analytical solution developed by Huang and Hu (2000). Based on the comparison results as discussed in Section 4, the following conclusions are reached:

1. The random walk particle-tracking technique developed in Section 3 is quite robust to simulate the conservative transport in heterogeneous dual-porosity media. The solute mass transfer process is fairly well simulated by the Markov chain model with the transitional probability matrix developed in Section 3. The Monte Carlo approach developed in this study provides a powerful tool to predict the spreading of the plume and long-term tailing behaviors of breakthrough curves as well. In addition, the Monte Carlo approach also provides uncertainty measurements associated with its predictions.
2. In comparison with the Monte Carlo simulation, the stochastic analytical solution developed by Huang and Hu (2000) is quite accurate for predicting transport in mild heterogeneous dual-porosity media. It provides a tool to evaluate the validity of the Monte Carlo simulation algorithm. Furthermore, the analytical solution also provides a powerful tool for sensitivity analysis required by most risk assessment studies.
3. In comparison with the Monte Carlo simulation, Huang and Hu's (2000) analytical solution is not applicable for predicting the transport in moderately and highly heterogeneous dual-porosity media. It overestimates the longitudinal spreading and underestimates the transverse spreading of the plume, especially at large travel time. It also overestimates the tailing behavior of breakthrough curves.

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