Mathematical Geology, Vol. 36, No. 2, February 2004 (© 2004)

Three-Dimensional Numerical Method of Moments for Linear Equilibrium-Adsorbing Solute Transport in Physically and Chemically Nonstationary Formations[1]

Jichun Wu[2,3] and Bill X. Hu[2,3,4]

A Lagrangian perturbation method is applied to develop a method of moments for reactive solute flux through a three-dimensional, nonstationary flow field. The flow nonstationarity may stem from medium nonstationarity, finite domain boundaries, and/or fluid pumping and injecting. The reactive solute flux is described as a space–time process where time refers to the solute flux breakthrough in a control plane at some distance downstream of the solute source and space refers to the transverse displacement distribution at the control plane. The analytically derived moments equations for solute transport in a nonstationary flow field are too complicated to solve analytically; therefore, a numerical finite difference method is implemented to obtain the solutions. This approach combines the stochastic model with the flexibility of the numerical method to boundary and initial conditions. The approach provides a tool to apply stochastic theory to reactive solute transport in complex subsurface environments. Several case studies have been conducted to investigate the influence of the physical and chemical heterogeneity of a medium on the reactive solute flux prediction in nonstationary flow field. It is found that both physical and chemical heterogeneity significantly affect solute transport behavior in a nonstationary flow field. The developed method is also applied to an environmental project for predicting solute flux in the saturated zone below the Yucca Mountain Project area, demonstrating the applicability of the method in practical environmental projects.

KEY WORDS: groundwater, stochastic methods, subsurface heterogeneity, nonstationarity, method of moments.

INTRODUCTION

It has been widely recognized that natural media are generally heterogeneous, which is shown in the dramatically spatial variations of hydraulic parameters such as hydraulic conductivity and the chemical sorption coefficient. Heterogeneity will significantly influence the flow and solute transport processes through the media. Owing to spatial variability of hydraulic parameters in natural media and scarcity

[1]Received 30 January 2003; accepted 14 October 2003.

[2]Desert Research Institute, Division of Hydrologic Sciences, University and Community College System of Nevada, Las Vegas, Nevada 89119.

[3]Department of Earth Sciences, Nanjing University, Nanjing, People's Republic of China.

[4]Hydrologic Sciences Program, University of Nevada, Reno, Nevada 89557; e-mail: hu@dri.edu

of available field data, these parameters are treated as spatial random variables. There are generally two approaches used in studying the influence of parameter randomness on flow and transport processes. One approach is the Monte Carlo method where multiple realizations of parameter distributions are generated. On the basis of the realizations, deterministic models or simulators such as MODFLOW and MT3D are used to generate the multiple realizations for the flow and transport prediction, where the means and variances are obtained through the statistical analysis from the realizations. Currently, the Monte Carlo method is widely applied in many environmental projects, especially in the transport uncertainty analysis. The results of this method are always approximations of the exact solutions in practical calculations, since unlimited realizations are required to obtain the exact solutions. Generally, for a study domain with one type of medium, hundreds of realizations are needed to obtain the converged mean results, such as the mean head, mean concentration or mean solute flux, and thousands of realizations are required to obtain the variances about the means. If a study domain contains two or more subdomains with different media, many more realizations are required to obtain the solutions. Generally, a large number of calculations are required to apply a Monte Carlo method in studying flow and transport in complicated heterogeneous media, and this requirement limits the application of the Monte Carlo method to environmental projects.

Another approach used to study the influence of parameter randomness on flow and transport processes is the stochastic perturbation approach where a correlation function is used to describe the statistical distribution of the conductivity field, and only "one" realization is needed to obtain the flow and solute transport solutions. In the last three decades, the stochastic perturbation method has been extensively applied to develop theories for flow and solute transport in heterogeneous media. However, most stochastic transport theories (e.g., Cushman, 1997; Dagan, 1982, 1984, 1989; Deng, Cushman, and Delleur, 1993; Gelhar, 1986; Gelhar and Axness, 1983; Naff, 1990; Neuman and Zhang, 1990; Winter, Newman, and Newman, 1984) are based on the following assumptions: (1) steady-state flow without boundaries; (2) constant mean flow velocity in space; (3) stationary permeability field; and (4) small variance of log-hydraulic conductivity. Although not realistic, these assumptions simplify calculations. However, these strict assumptions limit the application of stochastic theories to solute transport in complicated natural media, such as media with multiscale heterogeneity. This limitation poses a critical question regarding the development of stochastic theories: "How can stochastic theory be applied to predict groundwater flow and solute transport in practical environmental projects?"

Another issue concerning most stochastic theories is the lack of studies conducted on prediction uncertainty. The ensemble mean concentration, or its spatial moments, is the simplest property of a concentration field resulting from the selected ensemble and indisputably represents the most important property. However,

most research has focused on the mean concentration or its spatial moments alone. Probably the most unfortunate result is that, even today, many regulatory guidelines are still based on the mean calculation results alone, and very little attention has been given to the importance of other statistical properties of the concentration field, primarily the variance about the mean. At the same time, uncertainty in estimating cleanup costs is associated with the lack of detailed knowledge related to the spatial and temporal distribution of contaminants, as well as to the lack of knowledge regarding effectiveness of the remediation. These difficulties highlight the need for developing new modeling approaches to delineate the subsurface contaminant plume.

Recently, a three-dimensional numerical method of moments for modeling nonreactive solute transport in nonstationary heterogeneous media has been developed (Wu, Hu, and Zhang, 2003; Zhang and others, 2000) where a Lagrangian perturbation method is applied to develop the framework for solute transport in a nonstationary flow field and a numerical method is implemented to obtain the solution. In developing the theory, the assumptions listed for most stochastic theories are not required. The predicted quantities will be the mean of the solute mass flux through a control plane (CP) and the variance about the mean. The method is designed for realistic solute transport in a complicated natural media. In this study, we extended previous studies to include reactive solute transport in a physically and chemically nonstationary medium. The analytical moments equations are solved numerically with a finite difference method. This method combines the stochastic concept with the flexibility of a numerical method to complex boundary and initial conditions and provides a tool for applying stochastic theory to complex groundwater environments.

This paper is organized as follows. The physical and chemical nonstationarity of a medium is described in second section. The nonstationary velocity field is analyzed briefly in third section. Fourth section presents a generalized framework for solute mass flux through a CP located at some distance from the solute source. Fifth section describes how various moments of solute travel time and transverse displacement are related to groundwater flow in the integral or differential forms. These moments are then related to the probability density functions (PDF) of one and two parcels. Sixth section illustrates the approach with examples. The developed numerical method of moments is then applied to an environmental project for predicting solute flux in the saturated zone below the Yucca Mountain project area in seventh section. A summary of this study is provided in eighth section.

PHYSICAL AND CHEMICAL NONSTATIONARITY

As summarized by Zhang (2002), there are many different types of nonstationarity in natural media. In our current study, a common type of nonstationarity, zonal

stationarity, is considered. It has been observed frequently in the field that geologic formations include several distinct geologic units (e.g., layers, zones), which may have resulted from different geologic processes. Although the hydraulic conductivity and/or sorption coefficient of each geologic unit are stationary processes (fields), the geologic unit has different statistical moments from its neighboring units. Therefore, the hydraulic conductivity or sorption coefficient field of the entire formation is not stationary. Such a random field is called a zonally stationary field.

The nonstationarity of a log-hydraulic conductivity field, $Y(\boldsymbol{x}) = \ln K(\boldsymbol{x})$, may manifest in such ways; its mean, $\langle Y(\boldsymbol{x})\rangle$, and variance, $\sigma_Y^2(\mathbf{x})$, vary spatially, and its two-point covariance, $C_Y(\mathbf{x}, \chi)$, depends on the actual locations of $\boldsymbol{x}$ and χ. For a zonally stationary field, its mean, $\langle Y(\boldsymbol{x})\rangle$, and variance, $\sigma_Y^2(\mathbf{x})$, are fixed within each zone but vary from one zone to another. $C_Y(\mathbf{x}, \chi) = C_Y(\mathbf{x} - \chi)$ is stationary if $\boldsymbol{x}$ and χ are in same zone and is zero if $\boldsymbol{x}$ and χ are in different zones. Although $C_Y(\mathbf{x} - \chi)$ can take any form; we are considering only the exponential form for simplicity.

$$C_Y(\mathbf{x} - \chi) = \sigma_Y^2(\mathbf{x}) \exp\left\{-\left[\frac{(x_i - \chi_i)^2}{\lambda_i^2(\mathbf{x})}\right]^{1/2}\right\} \tag{1}$$

where i is the coordinate direction, $\lambda_i (i = 1, 2, 3)$ is the correlation length, and σ_Y^2 is the variance. The Einstein summation is applied in Equation (1).

Similar to hydraulic conductivity, the dramatically spatial variation of the chemical sorption coefficient, $K_d(\boldsymbol{x})$, has also been observed in field measurement (e.g., Brusseau, 1994). To account for spatial variability, we assume the retardation, $R(\boldsymbol{x}) = 1 + K_d(\boldsymbol{x})$, to be a random spatial variable. The distribution of $R(\boldsymbol{x})$ is also assumed to be zonally stationary, which means that the mean $\langle R(\boldsymbol{x})\rangle$ and variance σ_W^2 $(\mathbf{x})$ are fixed within a zone but vary zonally, and $C_R(\mathbf{x}, \chi) = C_R(\mathbf{x} - \chi)$ if $\mathbf{x}$ and χ are in the same region (medium); otherwise, $C_R(\mathbf{x}, \chi) = 0$.

The correlation between $Y(\boldsymbol{x})$ and $R(\boldsymbol{x})$ or $K_d(\boldsymbol{x})$ has been studied for many years; however, a general rule for the correlation does not exist. To investigate the effect of correlation on solute transport, theoretical models have been proposed to assume that $R(\mathbf{x})$ is either perfectly correlated or uncorrelated with the log-conductivity field, $Y(\mathbf{x})$ (Bellin and others, 1993; Destouni and Cvetkovic, 1991; Valocchi, 1989). Bellin and Rinaldo (1995) suggest that the model may be partially correlated rather than perfectly correlated or uncorrelated. In this study, three models are used in this study for the purpose of illustration (Bellin and others, 1993).

Perfect positive correlation (Model A):

$$R(\mathbf{x}) = 1 + K_d^G(\mathbf{x})\, e^{Y'(\mathbf{x})} \tag{2}$$

Perfect negative correlation (Model B):

$$R(\mathbf{x}) = 1 + K_d^G(\mathbf{x})\, e^{-Y'(\mathbf{x})} \tag{3}$$

No correlation (Model C):

$$R(\mathbf{x}) = 1 + K_d^G(\mathbf{x})\, e^{W'(\mathbf{x})} \tag{4}$$

where $K_d^G(\mathbf{x})$ is the geometric mean of $K_d(\mathbf{x})$ and $W'(\mathbf{x})$ is a normally distributed random space function with a mean of 0, variance $\sigma_W^2(\mathbf{x}$, and covariance function of

$$C_W(\mathbf{x} - \chi) = \sigma_W^2(\mathbf{x})\, \exp\left\{ -\left[\frac{(x_i - \chi_i)^2}{\lambda_{w,i}^2(\mathbf{x})} \right]^{1/2} \right\}$$

where $\boldsymbol{x}$ and χ are in the same zone and $\lambda_{w,i}$ is the correlation length along the x_i axis.

By expanding the exponential terms in the preceding Models A–C in the Taylor series, we can obtain the mean of the retardation factor in the first-order of σ_Y^2 or σ_w^2 as (Bellin and others, 1993):

Models A and B:

$$\langle R(\mathbf{x}) \rangle = 1 + K_d^G(\mathbf{x})\, e^{\left[\sigma_Y^2(\mathbf{x})/2\right]} \tag{5}$$

Model C:

$$\langle R(\mathbf{x}) \rangle = 1 + K_d^G(\mathbf{x})\, e^{\left[\sigma_W^2(\mathbf{x})/2\right]} \tag{6}$$

Similarly, the covariance is given by

Models A and B:

$$\begin{aligned} C_R(\mathbf{x}, \boldsymbol{\chi}) = C_R(\mathbf{x} - \boldsymbol{\chi}) &= [K_d^G(\mathbf{x})]^2\, e^{\sigma_Y^2(\mathbf{x})} [e^{C_Y(\mathbf{x}-\chi)} - 1] \\ &\quad (\boldsymbol{x} \text{ and } \chi \text{ are in the same zone}) \\ &= 0 (\boldsymbol{x} \text{ and } \chi \text{ are not in the same zone}) \end{aligned} \tag{7}$$

Model C:

$$\begin{aligned} C_R(\mathbf{x}, \chi) = C_R(\mathbf{x} - \chi) &= \left[K_d^G(\mathbf{x})\right]^2 e^{\sigma_W^2(\mathbf{x})} \left[e^{C_W(\mathbf{x}-\chi)} - 1\right] \\ &\quad (x \text{ and } \chi \text{ are in the same zone}) \\ &= 0\, (x \text{ and } \chi \text{ are not in the same zone}) \end{aligned} \tag{8}$$

For models A and B, the cross-covariance of $Y(\mathbf{x})$ and $R(\mathbf{x})$ is generally given by

$$C_{YR}(\mathbf{x}, \chi) = C_{YR}(\mathbf{x} - \chi) = \pm K_d^G(\mathbf{x})\, e^{\sigma_Y^2(\mathbf{x})/2} C_Y(\mathbf{x} - \chi) = C_{YR}(\chi, \mathbf{x})$$
$$(x \text{ and } \chi \text{ are in the same zone})$$
$$= 0 \ (x \text{ and } \chi \text{ are not in the same zone}) \qquad (9)$$

with the plus sign for Model A and the minus sign for Model B. For model C, $C_{YR}(\mathbf{x}, \chi) = 0$.

NONSTATIONARY VELOCITY FIELD

We consider incompressible groundwater flow in a heterogeneous aquifer with spatially variable hydraulic conductivity, groundwater seepage velocity, $\mathbf{V}(\mathbf{x})$, satisfies the continuity equation and Darcy's law,

$$\nabla \cdot \mathbf{V}(\mathbf{x}) = 0 \text{ and } V_i(\mathbf{x}) = -\frac{K(\mathbf{x})}{n} \frac{\partial h(\mathbf{x})}{\partial x_i},$$

subject to boundary conditions $h(\mathbf{x}) = H(\mathbf{x})_{\mathbf{x}} \in \Gamma_D$ and $\mathbf{V}(\mathbf{x}) \cdot \gamma(\mathbf{x}) = \Omega(\mathbf{x})\ \mathbf{x} \in \Gamma_N$, where $h(\mathbf{x})$ is hydraulic head, $K(\mathbf{x})$ is hydraulic conductivity (assumed to be isotropic locally), n is the porosity assumed to be constant, $H(\mathbf{x})$ is prescribed head on Dirichlet boundary segments Γ_N, $\Omega(\mathbf{x})$ is prescribed flux across Neumann boundary segments Γ_N, and $\gamma(\mathbf{x})$ is an outward unit vector normal to the boundary. In this study, $H(\mathbf{x})$ is assumed to be deterministic, and $\Omega(\mathbf{x})$ is assumed to be zero (no-flow boundary). Zhang and Winter (1999) developed a numerical moments approach for groundwater flow in a stationary conductivity field in a bounded domain. In this study, we extend the method to groundwater flow in nonstationary conductivity fields having internal and external boundary conditions. The resulting velocity moments will serve as the input data for the transport calculation. The method, which is similar to the work of Zhang and Winter (1999), will not be presented here. Basically, the method provides a way for calculating the mean and covariance (or variance) of hydraulic head, $\langle h(\mathbf{x}) \rangle$ and $C_h(\mathbf{x}, \chi)$; covariance between head and log-hydraulic conductivity, $C_{hY}(\mathbf{x}, \chi)$; and mean and covariance of velocity, $\langle V_i(\mathbf{x}) \rangle$ and $C_{v_{ij}}(\mathbf{x}, \chi)$, in the first-order accuracy of σ_Y^2 with the boundary conditions previously described.

In this study, we consider a reactive chemical transport under linear equilibrium sorption. The chemical sorption process will retard movement velocity of the reactive solute. The retarded velocity field is $V^R(\mathbf{x})$ is related to the groundwater

velocity as

$$V^R(\mathbf{x}) = \frac{V(\mathbf{x})}{R(\mathbf{x})} \tag{10}$$

Decompose $V(\mathbf{x})$ and $R(\mathbf{x})$ into their means and perturbations, $V(\mathbf{x}) = \langle V(\mathbf{x})\rangle + V'(\mathbf{x})$ and $R(\mathbf{x}) = \langle R(\mathbf{x})\rangle + R'(\mathbf{x})$, and insert them into Equation (10), then we can obtain the mean and variance of $V^R(\mathbf{x})$ in the zeroth- and first-order accuracy of σ_v^2 and/or σ_R^2, respectively, as

$$\langle V^R(\mathbf{x})\rangle = \frac{\langle V(\mathbf{x})\rangle}{\langle R(\mathbf{x})\rangle} \tag{11}$$

$$\begin{aligned} C^R_{v_{ij}}(\mathbf{x}, \chi) = {} & \frac{C_{v_{ij}}(\mathbf{x}, \chi)}{\langle R(\mathbf{x})\rangle\langle R(\chi)\rangle} + \frac{\langle V_i(\mathbf{x})\rangle\langle V_j(\chi)\rangle}{\langle R(\mathbf{x})\rangle^2\langle R(\chi)\rangle^2} C_R(\mathbf{x}, \chi) \\ & - \frac{\langle V_i(\mathbf{x})\rangle\langle V_j(\chi)\rangle}{\langle R(\mathbf{x})\rangle\langle R(\chi)\rangle^2} C_{YR}(\mathbf{x}, \chi) + \frac{\langle V_j(\chi)\rangle}{\langle R(\mathbf{x})\rangle\langle R(\chi)\rangle^2} \frac{K_{G_i}(\mathbf{x})}{n} \frac{\partial C_{hR}(\mathbf{x}, \chi)}{\partial x_i} \\ & - \frac{\langle V_i(\mathbf{x})\rangle\langle V_j(\chi)\rangle}{\langle R(\mathbf{x})\rangle^2\langle R(\chi)\rangle} C_{YR}(\chi, \mathbf{x}) + \frac{\langle V_i(\mathbf{x})\rangle}{\langle R(\mathbf{x})\rangle^2\langle R(\chi)\rangle} \frac{K_{G_j}(\chi)}{n} \frac{\partial C_{hR}(\chi, x)}{\partial \chi_j} \end{aligned} \tag{12}$$

where $C_{hR}(\mathbf{x}, \chi)$ is the cross-covariance between $h(\mathbf{x})$ and $R(\mathbf{x})$ that can be computed using a Taylor expansion in $R'(\mathbf{x})$ as

Models A and B (Bellin and others, 1993):

$$C_{hR}(\mathbf{x}, \chi) = \pm K_d^G(\chi) e^{[\sigma_Y^2(\chi)/2]} C_{hY}(\mathbf{x}, \chi) \tag{13a}$$

where the plus and minus signs are for Models A and B, respectively.
Model C:

$$C_{hR}(\mathbf{x}, \chi) = 0 \tag{13b}$$

Equation (12) is the general expression of the retarded velocity covariance with nonstationary fields of log-hydraulic conductivity and chemical sorption coefficient. Once the mean and variance of groundwater velocity are obtained, Equations (11) and (12) can be used to calculate the mean and variance of the retarded velocity. Owing to the nonstationarity of $V_i(\boldsymbol{x})$ and $R(\boldsymbol{x})$, a numerical method is required to solve $\langle V^R(\mathbf{x})\rangle$ and $C^R_{v_{ij}}(\mathbf{x}, \chi)$. In this study, a finite difference method is implemented into Equations (11) and (12). The calculated results will be used to calculate the solute transport process.

METHOD OF MOMENTS FOR REACTIVE SOLUTE FLUX IN A NONSTATIONARY MEDIUM

In this study, a Lagrangian perturbation method is applied to develop the theory for reactive transport in a physically and chemically nonstationary field. The theory is called a method of moments because the engine of the calculation is the various moments. The method of moments was developed for nonreactive solute flux in a physically nonstationary medium in previous studies (Wu, Hu, and Zhang, 2003, in press; Zhang and others, 2000). In this study, we will extend the method to study reactive chemical transport under linear equilibrium sorption with nonstationary distribution of sorption coefficient.

We consider reactive solute transport in a heterogeneous aquifer with spatially variable $K(\mathbf{x})$ and $K_d(\mathbf{x})$. The reactive solute is under linear equilibrium sorption, and the retarded movement velocity, $\boldsymbol{V}^R(\boldsymbol{x})$, is considered to be nonstationary caused by the physical and chemical medium nonstationarity and/or domain boundaries. A solute of total mass M is released into the flow field at time $t = 0$ over the injection area A_0 located at $x = 0$ either instantaneously or with a known release rate quantified by a rate function, $\phi(t)[T^{-1}]$. We denote with $\rho_0(\mathbf{a})[M/L^2]$ an areal density of injected solute mass at the location $\mathbf{a} \in A_0$. With $\Delta\mathbf{a}$ denoting an elementary area at $\mathbf{a}$, the parcel with mass, $\rho_0\Delta\mathbf{a}$, is advected by the random, spatially nonstationary groundwater retarded velocity $\boldsymbol{V}^R(\boldsymbol{x})$. For $t > 0$, a solute plume is formed and advected downstream by the flow field toward a (y, z)-plane, located at some distance from the source. The solute mass flux will be predicted or measured through the (y, x)-plane. The plane is referred to as the CP. Integrating the solute flux for a single parcel, $\Delta q \equiv \rho_0(\mathbf{a})d\mathbf{a}\phi(t-\tau)\delta(\mathbf{y}-\boldsymbol{\eta})$, over the injection area A_0 averaging over the sampling area $A(\mathbf{y})$ centered at $\mathbf{y}(y, z)$ yields the solute mass flux component orthogonal to CP at x as

$$q(t, \mathbf{y}; x, A) = \frac{1}{A}\int_{A_0}\int_{A}\rho_0(a)\phi(t-\tau)\delta(\mathbf{y}'-\boldsymbol{\eta})\,d\mathbf{y}'d\mathbf{a}$$

where $\tau \equiv \tau(x; \mathbf{a})$ is the travel time of the advective parcel from $\mathbf{a}$ to CP at x, and $\boldsymbol{\eta} \equiv (\eta, \xi)$, ($\eta \equiv \eta(x; \mathbf{a})$, and $\xi \equiv \xi(x; \mathbf{a})$) are the transverse locations of a parcel passing through CP. The τ and η are random variables and are functions of the underlying random velocity field.

The solute discharge is another quantity of interest and focus of this study. Solute discharge is defined as the total solute mass flux over the entire CP at x, whose mean and variance in the case of point sampling (i.e., $A \to 0$) are given as (Wu, Hu, and Zhang, 2003; Zhang and others, 2000)

$$\langle Q(t, x)\rangle = \int_{A_0}\int_{0}^{\infty}\rho_0(\mathbf{a})\phi(t-\tau)\,f_1[\tau(x, \mathbf{a}) = t]\,d\tau\,d\mathbf{a} \tag{14}$$

$$\sigma_Q^2(t, x) = \langle Q^2\rangle - \langle Q\rangle^2 \tag{15a}$$

and

$$\langle Q^2(t,x)\rangle = \int_A \int_A \int_0^\infty \int_0^\infty \rho_0(\mathbf{a})\rho_0(\mathbf{b})\phi(t-\tau_1)\phi(t-\tau_2)\, f_2[\tau_1(x,\mathbf{a}) = t;\tau_2(x,\mathbf{b}) = t]\, d\tau_1\, d\tau_2\, d\mathbf{a}\, d\mathbf{b} \tag{15b}$$

where $f_1[\tau(x,\mathbf{a})]$ is the PDF of the travel time τ for a parcel from a point $\mathbf{a}$ to reach CP, and $f_2[\tau_1(x,\mathbf{a});\tau_2(x,\mathbf{b})]$ is the two-parcel joint PDF of travel time. Similar to $\mathbf{a}$, here $\mathbf{b} \equiv (b_x, b_y, b_z)^T$ is the starting point of another parcel.

To evaluate the statistical moments of solute flux, one needs to know the one- and two-parcel PDFs, f_1 and f_2, or an infinite number of statistical moments. The approach used in this study is to evaluate a finite number of statistical moments and assume certain functions for f_1 and f_2. It has been found that it is not unreasonable to approximate travel time, τ, with a log-normal distribution and transverse displacement, η, as a normal distribution (Bellin, Rubin, and Rinaldo, 1994; Cvetkovic, Cheng, and Wen, 1996). On the basis of this assumption, the PDFs can be evaluated from the first two moments of $\tau(x;\mathbf{a})$ and $\boldsymbol{\eta}(x;\mathbf{a})$ as well as their joint moments.

In the Lagrangian frame, $\tau(x;\mathbf{a})$ and $\eta(x;\mathbf{a})$, can be related to the velocity field through (Andricevic and Cvetkovic, 1998; Zhang and others, 2000)

$$\frac{d\tau}{dx} = \frac{1}{V_1^R(x,\eta,\xi)}, \quad \frac{d\eta}{dx} = \frac{V_2^R(x,\eta,\xi)}{V_1^R(x,\eta,\xi)}, \quad \frac{d\zeta}{dx} = \frac{V_3^R(x,\eta,\xi)}{V_1^R(x,\eta,\xi)} \tag{16}$$

where $V_i^R(x,\eta,\xi)(i = 1,2,3)$ is the retarded Lagrangian velocity. Since the retarded Eulerian velocity, $\mathbf{V}^R(x,y,z)$, is a random variable, so are the Lagrangian velocity $V_i^R(x,\eta,\xi)$, travel time $\tau(x;\mathbf{a})$, and transverse displacements $\eta(x;\mathbf{a})$ and $\xi(x;\mathbf{a})$. We decompose the retarded Eulerian velocity as $\mathbf{V}^R(x,y,z) = \mathbf{U}^R(x,y,z) + \mathbf{u}^R(x,y,z)$ where $\mathbf{U}^R$ is the ensemble mean velocity and $\mathbf{u}^R$ is a zero-mean velocity fluctuation. For the retarded Lagrangian velocity, $\mathbf{V}^R[x,\eta(x;\mathbf{a}),\xi(x;\mathbf{a})]$, both the parcel transverse positions, η and ξ, and the retarded velocity, $\mathbf{V}^R$, at this location are random variables.

Travel Time Moments

We may expand the longitudinal retarded Lagrangian velocity, V_1^R, around its mean path $[x, \langle\eta(x;\mathbf{a})\rangle, \langle\xi(x;\mathbf{a})\rangle]$ in a Taylor series,

$$V_1^R(x,\eta,\xi) = U_1^R(x,\langle\eta\rangle,\langle\xi\rangle) + u_1^R(x,\langle\eta\rangle,\langle\xi\rangle)$$

$$+\eta'\frac{\partial\left[U_1^R(x,\eta,\xi)+u_1^R(x,\eta,\xi)\right]}{\partial\eta}\Big|_{\eta=\langle\eta\rangle}$$
$$+\xi'\frac{\partial\left[U_1^R(x,\eta,\xi)+u_1^R(x,\eta,\xi)\right]}{\partial\xi}\Big|_{\xi=\langle\xi\rangle}+\cdots \tag{17}$$

where $\eta'=\eta-\langle\eta\rangle$ and $\xi'=\xi-\langle\xi\rangle$ with $\langle\eta'\rangle=0$ and $\langle\xi'\rangle=0$. It is important to mention that in the classical stochastic theory (Dagan, 1982, 1984; Gelhar and Axness, 1983), the mean velocity, U_1^R, is constant, so that only the first two terms on the right-hand side of (17) exist. For nonstationary flow, the derivative of U_1^R is generally nonzero.

Travel time $\tau(L;\mathbf{a})$, the time required for a parcel originated at $\mathbf{a}$ to cross the plane $x=L$ in three dimension, can be expressed in Equation (17) as

$$\tau(L;\mathbf{a})=\int_{a_x}^{L}\frac{dx}{V_1^R[x,\eta(x;\mathbf{a}),\xi(x;\mathbf{a})]} \tag{18}$$

We may also decompose τ into its mean, $\langle\tau\rangle$, and fluctuation, τ'. With (17) and (18), we have the first-order of σ_Y^2 and σ_w^2,

$$\langle\tau(L;\mathbf{a})\rangle=\int_{a_x}^{L}\frac{dx}{U_1^R(x,\langle\eta\rangle,\langle\xi\rangle)} \tag{19}$$

$$\tau'(L;\mathbf{a})=-\int_{a_x}^{L}\frac{dx}{U_1^{R^2}(x,\langle\eta\rangle,\langle\xi\rangle)}\times\left[u_1^R(x,\langle\eta\rangle,\langle\xi\rangle)+g_1(x,\langle\eta\rangle,\langle\xi\rangle)\eta'+g_2(x,\langle\eta\rangle,\langle\xi\rangle)\xi'\right] \tag{20}$$

where $g_1(x,\langle\eta\rangle,\langle\xi\rangle)=\frac{\partial\lfloor U_1^R(x,\eta,\xi)\rfloor}{\partial\eta}\big|_{\substack{\eta=\langle\eta\rangle\\ \xi=\langle\xi\rangle}}$ and $g_2(x,\langle\eta\rangle,\langle\xi\rangle)=\frac{\partial\lfloor U_1^R(x,\eta,\xi)\rfloor}{\partial\xi}\big|_{\substack{\eta=\langle\eta\rangle\\ \xi=\langle\xi\rangle}}$. These expressions are derived up to the first-order and therefore require the coefficient of variation of velocity to be smaller than 1. This condition may be satisfied for many practical subsurface flows where the variance of log-transformed hydraulic conductivity is moderately large. With Equation (20), we obtain the two-parcel joint moment $\sigma_{\tau_1\tau_2}$ as

$$\sigma_{\tau_1\tau_2}(L;\mathbf{a};L;\mathbf{b})=\int_{a_x}^{L}\int_{b_x}^{L}\frac{dx_1\,dx_2}{U_1^{R^2}(x_1,\langle\eta_1\rangle,\langle\xi_1\rangle)U_1^{R^2}(x_2,\langle\eta_2\rangle,\langle\xi_2\rangle)}\times\Big[\big\langle u_1^R(x_1,\langle\eta_1\rangle,\langle\xi_1\rangle)u_1^R(x_2,\langle\eta_2\rangle,\langle\xi_2\rangle)\big\rangle+g_1(x_1,\langle\eta_1\rangle,\langle\xi_1\rangle)g_1(x_2,\langle\eta_2\rangle,\langle\xi_2\rangle)\langle\eta_1'\eta_2'\rangle+g_2(x_1,\langle\eta_1\rangle,\langle\xi_1\rangle)g_2(x_2,\langle\eta_2\rangle,\langle\xi_2\rangle)\langle\xi_1'\xi_2'\rangle$$

$$
\begin{aligned}
&+ g_1(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle u_1^R(x_2, \langle\eta_2\rangle, \langle\xi_2\rangle)\eta_1'\rangle \\
&+ g_1(x_2, \langle\eta_2\rangle, \langle\xi_2\rangle)\langle u_1^R(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\eta_2'\rangle \\
&+ g_2(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle u_1^R(x_2, \langle\eta_2\rangle, \langle\xi_2\rangle)\xi_1'\rangle \\
&+ g_2(x_2, \langle\eta_2\rangle, \langle\xi_2\rangle)\langle u_1^R(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\xi_2'\rangle \\
&+ g_1(x_2, \langle\eta_2\rangle, \langle\xi_2\rangle)g_2(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle\eta_2'\xi_1'\rangle \\
&+ g_1(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)g_2(x_2, \langle\eta_2\rangle, \langle\xi_2\rangle)\langle\eta_1'\xi_2'\rangle\big] \qquad (21)
\end{aligned}
$$

where $\eta_1 = \eta(x_1; \mathbf{a})$ and $\eta_2 = \eta(x_2; \mathbf{b})$. It is seen that by setting $\mathbf{b} = \mathbf{a}$, one can obtain $\sigma_\tau^2(L; \mathbf{a})$. It can be seen from Equation (21) that one needs to know the autovariances of η, ξ, and u_1^R and the covariances among them.

Transverse Location Moments

We will now examine the process for deriving the statistical moments for η and ξ. We may similarly expand the transverse retarded Lagrangian velocities, $V_j^R (j = 2, 3)$, around their mean path $[x, \langle\eta(x; \mathbf{a})\rangle, \langle\xi(x; \mathbf{a})\rangle]$, then substitute them with Equation (17) into Equation (15) to obtain, in the first-order,

$$
\frac{d\langle\eta(x; \mathbf{a})\rangle}{dx} = \frac{U_2^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \qquad (22)
$$

$$
\frac{d\langle\xi(x; \mathbf{a})\rangle}{dx} = \frac{U_3^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \qquad (23)
$$

$$
\begin{aligned}
\frac{d\eta'(x; \mathbf{a})}{dx} &= A_1(x, \langle\eta\rangle, \langle\xi\rangle)u_1^R(x, \langle\eta\rangle, \langle\xi\rangle) + B(x, \langle\eta\rangle, \langle\xi\rangle)u_2^R(x, \langle\eta\rangle, \langle\xi\rangle) \\
&\quad + C_1(x, \langle\eta\rangle, \langle\xi\rangle)\eta'(x; \mathbf{a}) + D_1(x, \langle\eta\rangle, \langle\xi\rangle)\xi'(x; \mathbf{a}) \qquad (24)
\end{aligned}
$$

and

$$
\begin{aligned}
\frac{d\xi'(x; \mathbf{a})}{dx} &= A_2(x, \langle\eta\rangle, \langle\xi\rangle)u_1^R(x, \langle\eta\rangle, \langle\xi\rangle) + B(x, \langle\eta\rangle, \langle\xi\rangle)u_3^R(x, \langle\eta\rangle, \langle\xi\rangle) \\
&\quad + C_2(x, \langle\eta\rangle, \langle\xi\rangle)\eta'(x; \mathbf{a}) + D_2(x, \langle\eta\rangle, \langle\xi\rangle)\xi'(x; \mathbf{a}) \qquad (25)
\end{aligned}
$$

where

$$
A_1(x, \langle\eta\rangle, \langle\xi\rangle) = -\frac{U_2^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^{R^2}(x, \langle\eta\rangle, \langle\xi\rangle)} \qquad (26a)
$$

$$A_2(x, \langle\eta\rangle, \langle\xi\rangle) = -\frac{U_3^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^{R^2}(x, \langle\eta\rangle, \langle\xi\rangle)} \tag{26b}$$

$$B(x, \langle\eta\rangle, \langle\xi\rangle) = \frac{1}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \tag{26c}$$

$$C_1(x, \langle\eta\rangle, \langle\xi\rangle) = \frac{\partial U_2^R(x, \eta, \xi)}{\partial \eta}\Big|_{\eta=\langle\eta\rangle} - \frac{U_2^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \frac{\partial U_1^R(x, \eta, \xi)}{\partial \eta}\Big|_{\eta=\langle\eta\rangle} \tag{26d}$$

$$C_2(x, \langle\eta\rangle, \langle\xi\rangle) = \frac{\partial U_3^R(x, \eta, \xi)}{\partial \eta}\Big|_{\eta=\langle\eta\rangle} - \frac{U_3^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \frac{\partial U_1^R(x, \eta, \xi)}{\partial \eta}\Big|_{\eta=\langle\eta\rangle} \tag{26e}$$

$$D_1(x, \langle\eta\rangle, \langle\xi\rangle) = \frac{\partial U_2^R(x, \eta, \xi)}{\partial \xi}\Big|_{\xi=\langle\xi\rangle} - \frac{U_2^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \frac{\partial U_1^R(x, \eta, \xi)}{\partial \xi}\Big|_{\xi=\langle\xi\rangle} \tag{26f}$$

and

$$D_2(x, \langle\eta\rangle, \langle\xi\rangle) = \frac{\partial U_3^R(x, \eta, \xi)}{\partial \xi}\Big|_{\xi=\langle\xi\rangle} - \frac{U_3^R(x, \langle\eta\rangle, \langle\xi\rangle)}{U_1^R(x, \langle\eta\rangle, \langle\xi\rangle)} \frac{\partial U_1^R(x, \eta, \xi)}{\partial \xi}\Big|_{\xi=\langle\xi\rangle} \tag{26g}$$

We use Equations (24) and (25) to obtain the expressions of autocovariances of η and ξ and the covariances among η, ξ, u_1^R, u_2^R, and u_3^R.

Multiplying Equation (24) by $\eta'(x_2; \mathbf{b})$ taking expectation and neglect high-order terms, we obtain

$$\begin{aligned}\frac{d\langle\eta'(x_1; \mathbf{a})\eta'(x_2; \mathbf{b})\rangle}{dx_1} &= A_1(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle u_1^R(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\eta'(x_2; \mathbf{b})\rangle \\ &+ B(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle u_2^R(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\eta'(x_2; \mathbf{b})\rangle \\ &+ C_1(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle\eta'(x_1; \mathbf{a})\eta'(x_2; \mathbf{b})\rangle \\ &+ D_1(x_1, \langle\eta_1\rangle, \langle\xi_1\rangle)\langle\xi'(x_1; \mathbf{a})\eta'(x_2; \mathbf{b})\rangle \end{aligned} \tag{27}$$

Similarly, we can also obtain the expressions of $\langle\eta'\xi'\rangle$, $\langle\xi'\xi'\rangle$, $\langle u_1^R\eta'\rangle$, $\langle u_1^R\xi'\rangle$, $\langle u_2^R\eta'\rangle$, $\langle u_2^R\xi'\rangle$, $\langle u_3^R\eta'\rangle$, and $\langle u_3^R\xi'\rangle$. For brevity, they are not shown here. The velocity correlations, $\langle u_i^R u_j^R\rangle (i = 1, 2, 3; j = 1, 2, 3)$, can be obtained from the velocity field and are treated as known quantities or input data here. Owing to the complexity of these equations, they are solved numerically.

Joint Moments of Travel Time and Transverse Locations

From Equation (20), the joint moments, $\langle \tau_1'(x_1;\mathbf{a})\eta_2'(x_2;\mathbf{b})\rangle$, can be given as

$$\langle \tau_1'(x_1;\mathbf{a})\eta_2'(x_2;\mathbf{b})\rangle = -\int_{a_x}^{x_1} \frac{d\chi}{U_1^{R^2}(\chi,\langle\eta\rangle,\langle\xi\rangle)}\Big[\big\langle u_1^R(\chi,\langle\eta\rangle,\langle\xi\rangle)\eta_2'(x_2;\mathbf{b})\big\rangle > + g_1(\chi,\langle\eta\rangle,\langle\xi\rangle)\langle\eta'(\chi;\mathbf{a})\eta_2'(x_2;\mathbf{b})\rangle > + g_2(\chi,\langle\eta\rangle,\langle\xi\rangle)\langle\xi'(\chi;\mathbf{a})\eta_2'(x_2;\mathbf{b})\rangle\Big] \quad (28)$$

In the same approach, we can also obtain the expression of $\langle \tau_1'(x_1;\mathbf{a})\xi_2'(x_2;\mathbf{b})\rangle$. Similar to the calculation of the travel–time moments, the calculations of the joint moments also require the various transverse moments as the input data, which in turn, require the mean velocity and velocity covariances as the known quantities.

Expressions for Probability Density Functions

To evaluate the statistical moments of solute flux, knowledge of the one- and two-parcel PDFs, f_1 and f_2, or an infinite number of statistical moments is required. Our approach to this Lagrangian closure problem is to evaluate a finite number of statistical moments and assume certain distributions of f_1 and f_2. In this study, we assume the travel time, τ, obeys a lognormal distribution, and transverse displacements, η and ξ, satisfy normal distributions. These assumptions are consistent with the previous numerical studies (Bellin, Rubin, and Rinaldo, 1994; Cvetkovic, Cheng, and Wen, 1996; Zhang and others, 2000). Under these assumptions, one- and two-parcel PDFs, f_1 and f_2, can be obtained and the expressions are the same as those obtained by Zhang and others (2000) and Wu, Hu, and Zhang (2003, in press). These expressions will not be given in this paper for brevity.

The complexity of the flow and transport moments equations precludes the possibility of using analytical methods to obtain their solutions except under some special conditions such as those required in the traditional stochastic theories (Dagan, 1982, 1984; Gelhar and Axness, 1983): a stationary flow field, no boundary influence, and simple initial condition. In general, numerical methods are required to obtain the solutions. Similar to the numerical solution to flow moment equations, the finite difference method is also applied to numerically solve the transport equations. In the following case studies, we will show the results calculated through the numerical method of moments.

SYNTHETIC CASE STUDIES

In this section, we illustrate our approach through several synthetic case studies. We focus on the combined effects of the physical and chemical nonstationarity on predicting the reactive solute flux and associate uncertainty.

Figure 1(a) is a sketch of the study domain, a small cube, called Cube A, measuring $5\lambda \times 5\lambda \times 5\lambda$ located at the center of a larger cube with the size $10\lambda \times 10\lambda \times 10\lambda$, where λ is the log-conductivity correlation length, and the two cubes are parallel with each other. The spatial distributions of hydraulic and chemical properties in one of the two subdomains (the small cube is subdomain 2, and the rest part of the study domain is subdomain 1) are statistically homogeneous, but the distributions in the two subdomains may be statistically different. A $1\lambda \times 1\lambda$ areal solute source with uniform density and unit mass is located at *yz*-plane centered at the point $(0.5\lambda, 5\lambda, 5\lambda)$. The source is represented by 5×5 uniformly distributed parcels. The CP is located at $x = 9.1\lambda$. The hydraulic boundary conditions of the box domain are specified as follows: constant hydraulic head ($h = 10\lambda$) for the left side ($x = 0$), constant hydraulic head ($h = 0$) for the right side ($x = 10\lambda$), and no-flow for the other four boundary sides. Therefore, the gradient across the domain is 1. Since there are several factors influencing the reactive transport processes, such as the means, variances, correlation lengths of hydraulic conductivity and sorption coefficient, and correlations between hydraulic conductivity and sorption coefficient, 14 specific cases, shown in Table 1, are proposed to study the influences of these factors on flow and transport processes.

The groundwater flow fields for all cases are calculated. For the purpose of illustration and brevity, the results of case 1 shown in Figure 1(b) are used to exhibit the nonstationary flow fields. One can see from the figure that the existence of Cube A results in significant changes to the mean flow in both direction and magnitude, which leads to flow nonstationarity in the domain.

Figure 2(a) and 2(b) presents the effects of the mean sorption coefficient and medium nonstationarity on mean and variance of solute flux. In cases 1 and 2, the distribution of log-hydraulic conductivity is nonstationary, but distribution of the chemical sorption coefficient is stationary. It is shown from the mean breakthrough results of the two cases that longitudinal plume dispersion increases with the increase of K_d^G, which is consistent with the results of Bosma and others (1993) for a stationary medium. This phenomenon can be explained from Equation (8): the variance of sorption coefficient increases with the increase of K_d^G. In cases 3 and 4, the distributions of sorption coefficient are the same and nonstationary. The distribution of log conductivity in case 4 is the same as in cases 1 and 2, but the distribution of log conductivity is stationary in case 3. The mean breakthrough results of the two cases show that the plume longitudinal dispersion is enhanced by the physical nonstationarity. In comparing results of cases 1, 2, and 4, the breakthrough in case 4 is between the two stationary cases, which show the influence

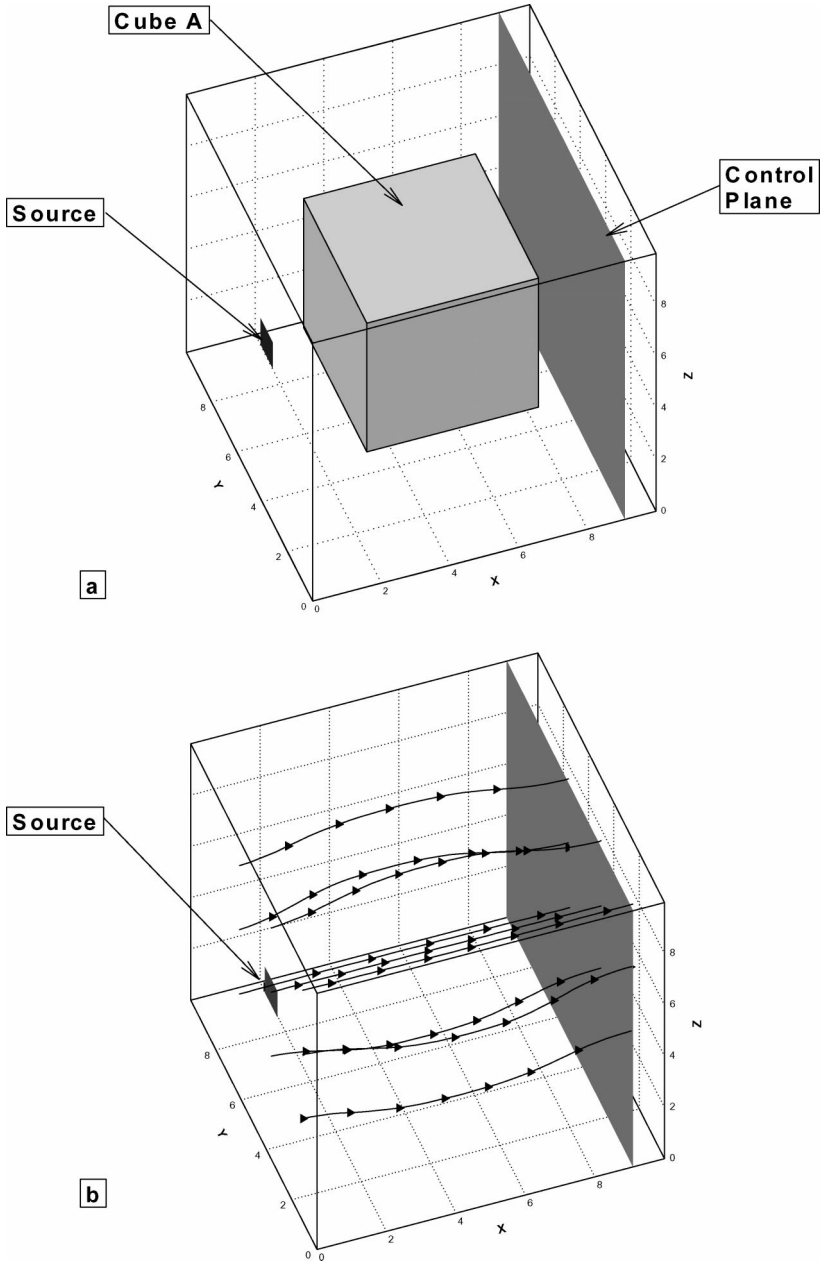

Figure 1. (a) Sketch of the research domain, locations of source and CP, and small Cube A; (b) flow field of case 1.

Table 1. Computation Cases for Nonstationary Flow Field

Case	Y_1	Y_2	$\sigma^2_{Y_1}$	$\sigma^2_{Y_2}$	λ_{Y_1} (m)	λ_{Y_2} (m)	$K^G_{d_1}$	$K^G_{d_2}$	$\sigma^2_{W_1}$	$\sigma^2_{W_2}$	λ_{W_1} (m)	λ_{W_2} (m)	Correlation
1	1.0	−1.0	0.8	0.8	1.0	1.0	2.0	2.0	0.8	0.8	1.0	1.0	Uncorrelated
2	1.0	−1.0	0.8	0.8	1.0	1.0	4.0	4.0	0.8	0.8	1.0	1.0	Uncorrelated
3	0.0	0.0	0.8	0.8	1.0	1.0	2.0	4.0	0.8	0.8	1.0	1.0	Uncorrelated
4	1.0	−1.0	0.8	0.8	1.0	1.0	2.0	4.0	0.8	0.8	1.0	1.0	Uncorrelated
5	1.0	−1.0	0.8	0.8	1.0	1.0	2.0	4.0	0.2	0.2	1.0	1.0	Uncorrelated
6	1.0	−1.0	0.8	0.8	1.0	1.0	2.0	4.0	0.2	0.8	1.0	1.0	Uncorrelated
7	1.0	−1.0	0.2	0.2	1.0	1.0	2.0	4.0	0.2	0.8	1.0	1.0	Uncorrelated
8	1.0	−1.0	0.2	0.8	1.0	1.0	2.0	4.0	0.2	0.8	1.0	1.0	Uncorrelated
9	1.0	−1.0	0.2	0.8	1.0	1.0	2.0	4.0	0.2	0.8	0.2	0.2	Uncorrelated
10	1.0	−1.0	0.2	0.8	1.0	1.0	2.0	4.0	0.2	0.8	0.2	1.0	Uncorrelated
11	1.0	−1.0	0.2	0.8	0.2	0.2	2.0	4.0	0.2	0.8	0.2	1.0	Uncorrelated
12	1.0	−1.0	0.2	0.8	0.2	1.0	2.0	4.0	0.2	0.8	0.2	1.0	Uncorrelated
13	1.0	−1.0	0.2	0.8	0.2	1.0	2.0	4.0	0.2	0.8	0.2	1.0	Positive
14	1.0	−1.0	0.2	0.8	0.2	1.0	2.0	4.0	0.2	0.8	0.2	1.0	Negative

of K_d^G on the transport process. The results in Figure 2(a) and 2(b) also show that the shape of the breakthrough curve σ_Q is similar to that of $\langle Q \rangle$ but with a larger value.

The variances of the sorption coefficient and log-hydraulic conductivity are used to describe the degrees of small-scale chemical and physical heterogeneity, respectively. Figure 3 is used to present the influences of the two kinds of heterogeneity on breakthrough curves of solute flux. The results of cases 4, 5, and 6 show that the solute dispersion increases with the increase of σ_w^2, and the results of cases 6, 7, and 8 indicate the solute dispersion also increases with the increase of σ_Y^2. The influence of σ_w^2 on the breakthrough curves is more obvious than the influence of σ_Y^2. Interestingly, variations of σ_W^2 or σ_Y^2 in the rest part of the study domain except Cube A has minor impact on spreading in the longitudinal direction (comparing results of case 4 with 6 and case 6 with 8), which implies that the hydraulic and chemical properties of the medium in Cube A play a far greater influence on the solute transport process than in the rest part of the study domain. This is because Cube A is placed along the solute pathway and occupies a significant portion of the pathway.

The correlation length is an important parameter in describing the spatial structure of a spatially variable property. Figure 4 presents the effects of correlation lengths of log-hydraulic conductivity and sorption coefficients on breakthrough curves of solute flux. The results of cases 8 and 9 show that the solute dispersion decreases with decreased λ_W. The results of cases 10 and 11 indicate that dispersion also decreases with decreased λ_Y. Similar to the finding in Figure 3, variations of λ_W or λ_Y in the rest part of the study domain except for Cube A has little impact on the spreading of solute flux in the longitudinal direction

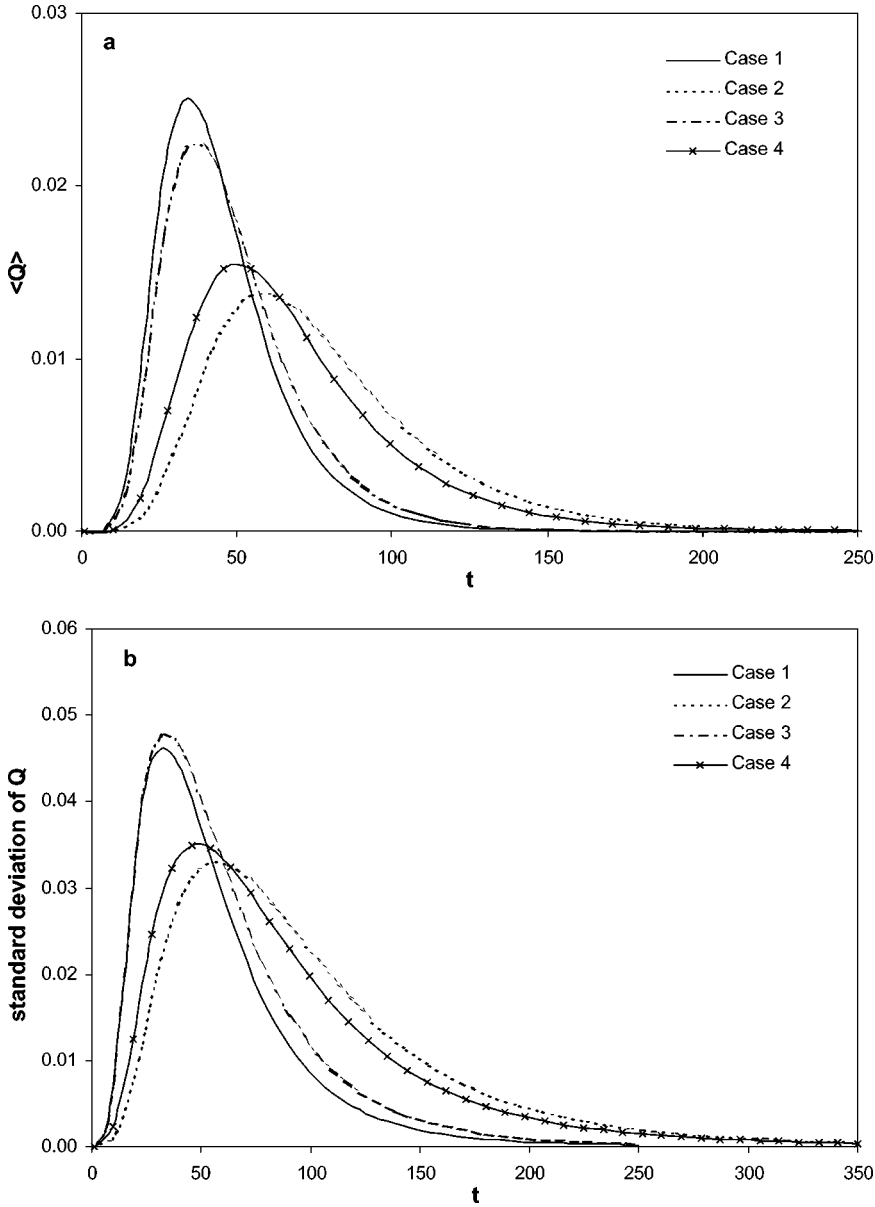

Figure 2. Breakthrough curves of solute flux, Q, through the CP at $x = 9.1\lambda$ with various mean sorption coefficient and hydraulic conductivity for nonstationary flow field: (a) expected value, $\langle Q \rangle$, and (b) standard deviation value σ_Q.

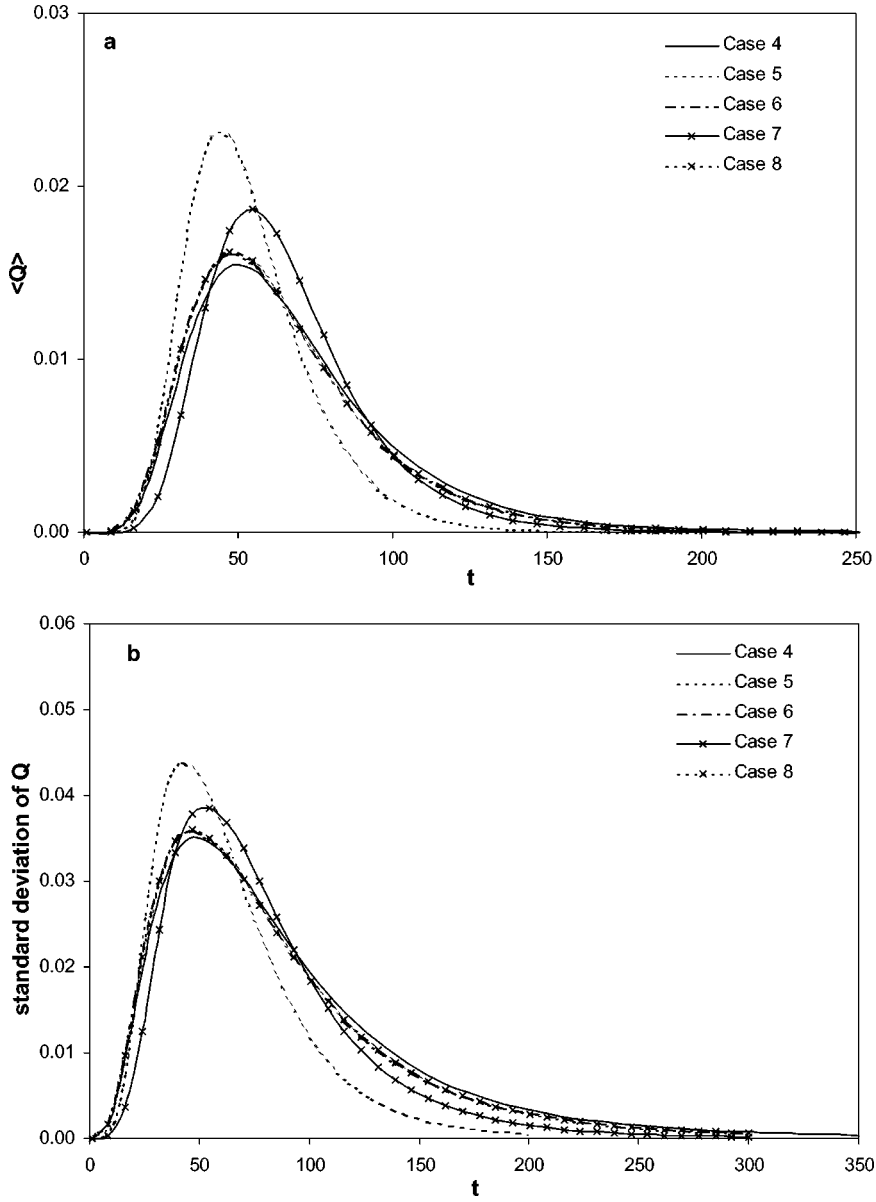

Figure 3. Breakthrough curves of solute flux, Q, through the CP at $x = 9.1\lambda$ with various variance values of the sorption coefficient and hydraulic conductivity for nonstationary flow field: (a) expected value, $\langle Q \rangle$, and (b) standard deviation value, σ_Q.

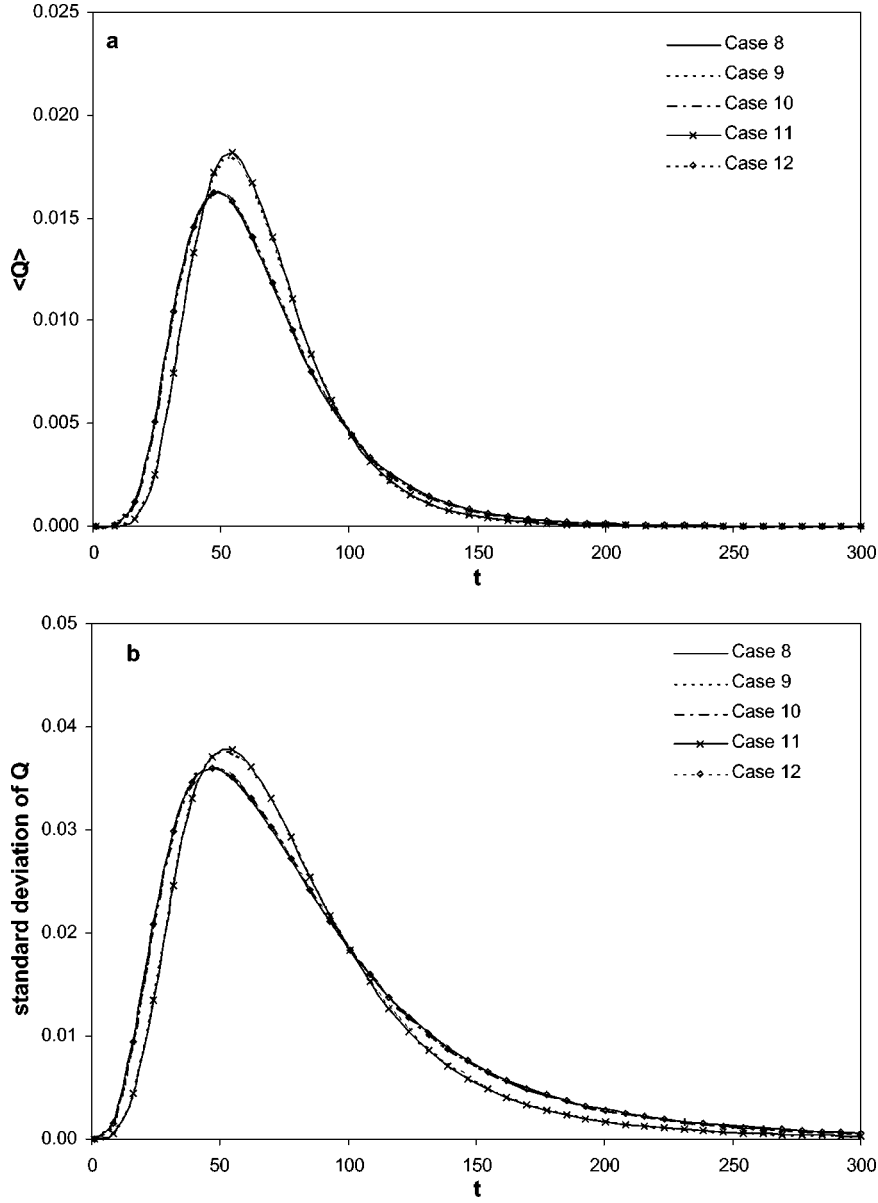

Figure 4. Breakthrough curves of solute flux, Q, through the CP at $x = 9.1\lambda$ with various correlation length values of the sorption coefficient and hydraulic conductivity for nonstationary flow field: (a) expected value, $\langle Q \rangle$, and (b) standard deviation value, σ_Q.

(solute flux distributions in cases 8, 10, and 12 are almost identical), which indicates again that the property of Cube A dominates the spreading process in the case studies.

Results shown in Figures 2, 3, and 4 were obtained under the assumption that there is not a correlation between the sorption coefficient and log-hydraulic conductivity (Model C). Figure 5 shows the influence of various correlations between the two parameters on the solute transport process. The negative correlation will enhance spreading of the plume in the longitudinal direction, while the positive correlation will decrease spreading. These results are consistent with those obtained for stationary media (Bosma and others, 1993; Hu, Deng, and Cushman, 1995). Although the peak times of three mean breakthrough curves are different, the plume mean breakthrough times are the same.

APPLICATION TO YUCCA MOUNTAIN PROJECT

Yucca Mountain is located in the Great Basin about 150 km northwest of Las Vegas, Nevada, in the United States. The mountain consists of a series of fault-bounded blocks of ash-flow and ash-fall tuffs and a smaller volume of lava deposited between 11 and 14 Ma (million years) ago from a series of calderas located a few to several tens of kilometers to the north. Yucca Mountain was chosen by the U.S. Department of Energy as a candidate site for storing high-level radioactive wastes. Many numerical studies have been conducted to simulate the potential solute transport process of radioactive wastes migrating from the repository to the groundwater (Zyvoloski and others, 1997). The saturated medium is composed of many layers of different materials, possessing quite different physical properties (e.g., hydraulic conductivity, etc.) and different chemical properties (e.g., sorption coefficient, etc.). Even within a single layer, significant spatial heterogeneity of hydraulic conductivity has been observed (Shirley, Pohlmann, and Andricevic, 1997). However, owing to the tremendous computational demand in conducting Monte Carlo simulations to study the influence of heterogeneity within each layer on groundwater flow and solute transport, current numerical modeling efforts are limited to the deterministic approach with effective parameter values, such as mean conductivity, macrodispersivity, and sorption coefficient. The deterministic approach predicts the mean or expected flow and solute transport processes, but it cannot fully address the uncertainties in the expected predictions. Here, we use the moments method to address these uncertainties.

The study domain, shown in Figure 6, measures 5500×5000 m horizontally and 990 m vertically. There are seven zones within this domain. The means, variances, and correlation lengths of the log conductivity and sorption coefficient within each zone are listed in Table 2. The log conductivity and sorption coefficient in each zone are assumed to take an isotropic exponential covariance, and no correlation is assumed between different zones (Fig. 6(a)). The right and left sides are

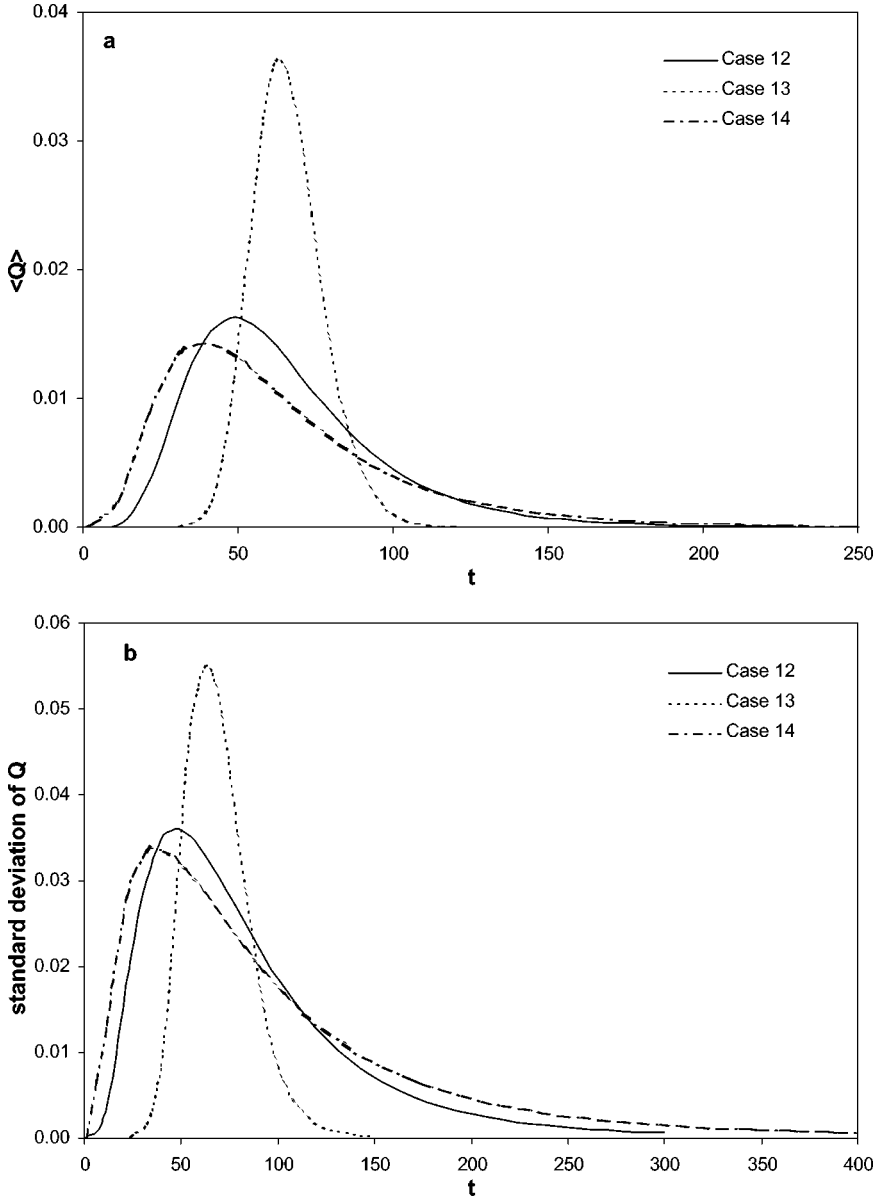

Figure 5. Breakthrough curves of solute flux, Q, through the CP at $x = 9.1\lambda$ with different correlation between $K(\mathbf{x})$ and $K_d(\mathbf{x})$ for nonstationary flow field: (a) expected value, $\langle Q \rangle$, and (b) standard deviation value, σ_Q.

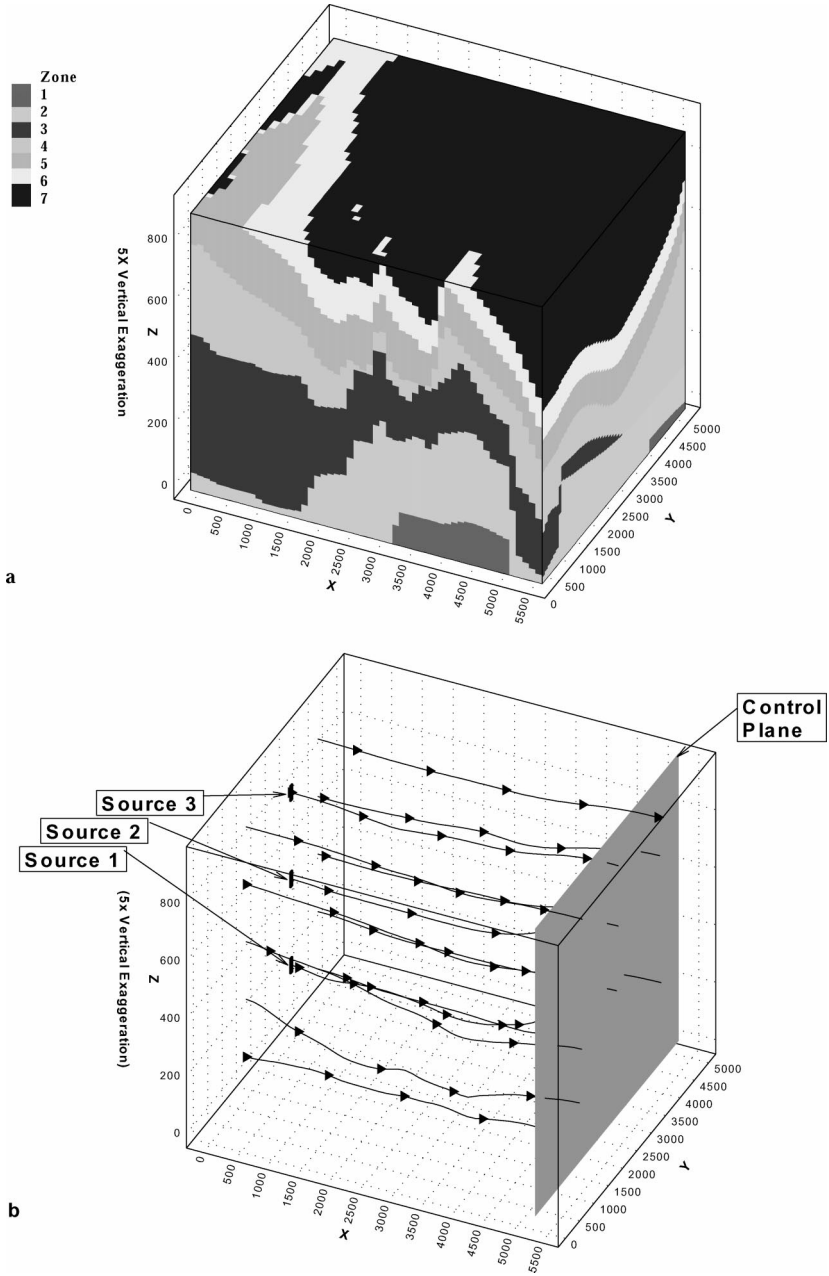

Figure 6. (a) Sketch of the study domain and distribution of different conductivity and sorption coefficient zones; (b) flow field with the locations of source and CP.

Table 2. Parameters of Each Zone in the Study Domain

Zone	Y	σ_Y^2	λ_Y(m)	K_d^G	σ_W^2	λ_W(m)
1	−0.81	1.63	550	0.1	0.1	100
2	−0.08	0.17	350	0.2	0.2	200
3	−0.24	0.48	650	0.3	0.3	300
4	−0.19	0.38	550	0.4	0.4	400
5	−0.12	0.25	500	0.5	0.5	500
6	−2.79	5.59	300	0.55	0.55	550
7	−0.92	1.84	250	0.6	0.6	600

constant heads at 736 m and 1000 m, respectively, and the other four boundaries are no-flow. The source area measures 50 × 50 m and is close to the left boundary. Three different locations of the source plane, shown in Figure 6(a), are chosen for a sensitivity study. The CP is fixed near the right boundary. The irregularity of flow lines is caused by the rough layer boundaries and large difference of mean permeability between the zones (Fig. 6(b)).

Figure 7(a) and 7(b) shows the mean solute breakthrough curves and variances about the means for reactive and nonreactive solute with the source area at different locations. The perfectly uncorrelated model is taken for the correlation between $\log K(\boldsymbol{x})$ and $K_d(\mathbf{x})$. It is shown in Figure 7 that the solute travels fastest when the source is at location 3 and slowest at location 1. This is consistent with the flow-line trajectory. When the solute transport is in a high-conductivity layer, the solute has a quick mean movement and small dispersion. Although not shown in Figure 7, it should be pointed out that with increased source area, solute dispersion significantly increases owing to the strong heterogeneity in the vertical direction. The predicted variance values are significantly larger than the mean values, which indicate that the mean prediction may significantly deviate from the real solute transport. To decrease the variance, conditioning on field measurements is required. Although used values of the mean sorption coefficient are small, the effect of sorption is apparent. The sorption renders the later arrival time and increased plume dispersion in the longitudinal direction. It also results in the greater difference between the various results having different source locations. The results in Figures 6 and 7 exhibit the flexibility of the moment method to solute transport in complex flow conditions.

SUMMARY

In this study, we developed a solute transport theory for reactive solute flux through three-dimensional, spatially nonstationary flow fields in porous media. The flow nonstationarity results from the nonstationary conductivity field and hydraulic boundary conditions. For reactive solute transport, nonstationarity may also stem

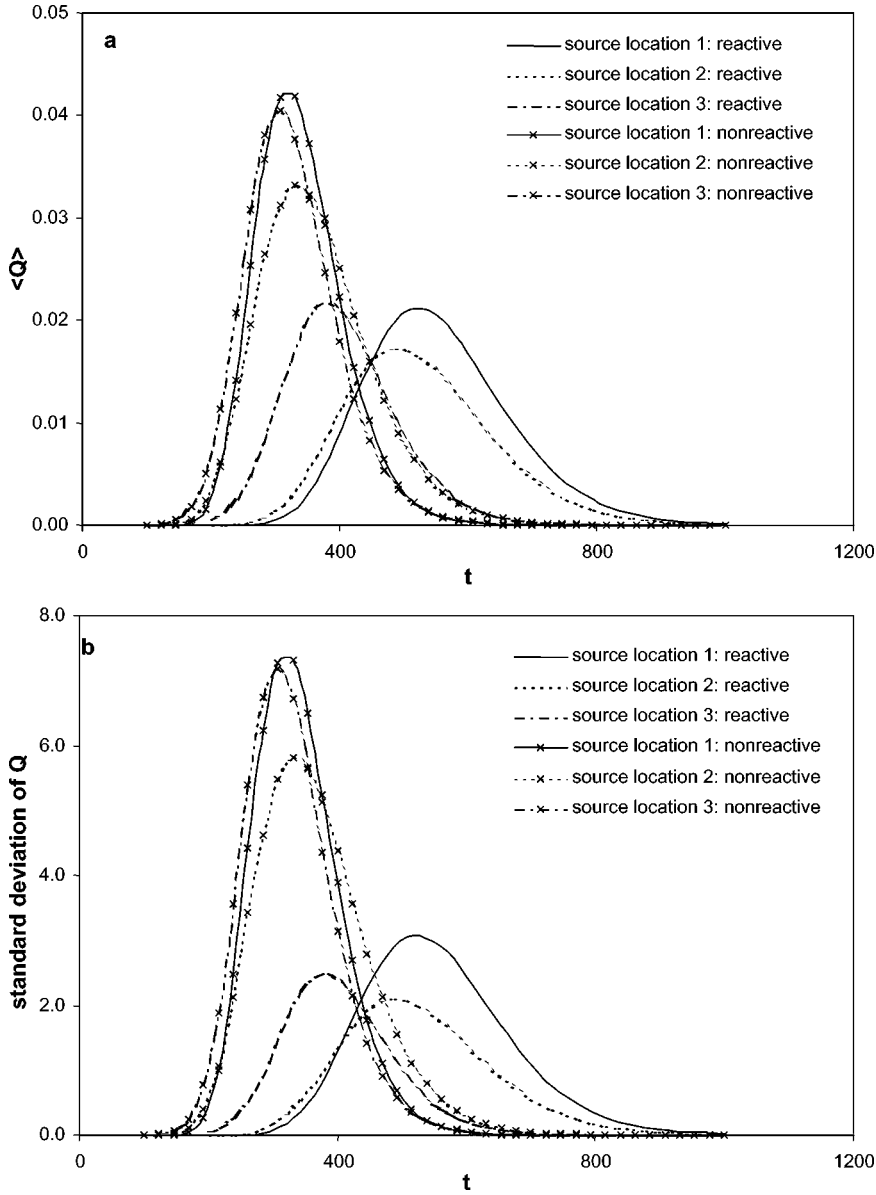

Figure 7. Solute breakthrough curves of total solute flux, Q, for reactive and nonreactive solute transport under various source locations: (a) expected value, $\langle Q \rangle$ and (b) standard deviation value, σ_Q.

from the distribution of sorption coefficient. These nonstationarity cases are not within the scope of the classical stochastic theory (Dagan, 1982, 1984; Gelhar and Axness, 1983) but exist widely in natural fields. We applied a Lagrangian perturbation method to analytically develop a stochastic framework for the mean and variance of solute flux in a physically and chemically nonstationary flow field. The development of the theory is based on the assumption that distribution of each parcel during the transport process satisfies a log-normal distribution in the longitudinal direction and a normal distribution in transverse directions. Under this assumption, the solute flux distribution can be calculated with the means and variances of the travel time of each parcel through the CP and transverse location on the CP. These means and variances are related to the mean and covariance of the retarded velocity field, which in turn is related to the conductivity field through Darcy's law. Owing to the complexity of the stochastic governing equations for flow and transport and the complex boundary conditions, numerical methods are implemented to obtain the solutions.

The general approach was illustrated with synthetic examples of reactive transport in nonstationary media. The examples were used to investigate the influences of various factors on the solute transport process. These factors include mean values of log-hydraulic conductivity and sorption coefficients in the two subdomains, variances, and correlation lengths of log-hydraulic conductivity and sorption coefficients. These factors also include the relationship between the two parameters—log-hydraulic conductivity and sorption coefficients. The sensitivity studies show that all factors will significantly influence the solute transport processes.

The method of moments is applied to study potential solute transport in groundwater below the Yucca Mountain Project area. Although the used values of mean sorption coefficient are small, the effect of sorption is apparent. It is shown that the method is applicable to situations with complex flow and solute transport conditions. In comparison with Monte Carlo numerical simulation method, only one "realization" is needed to obtain the solutions, while a large number of realizations are demanded in the Monte Carlo method.

The variance of solute flux is generally larger than its mean value, which indicates that the mean prediction may seriously deviate from the real transport process. This result is consistent with previous studies on solute transport in stationary media through the method of moments or Monte Carlo simulation method. Conditioning on field measurements is required to reduce uncertainty.

ACKNOWLEDGMENTS

This work was partially funded by U.S. Department of Energy (DOE), Yucca Mountain Project, under contract between DOE and the University and Community College System of Nevada; National Science Foundation of China (Project Number

40272106), and Teaching and Research Award Program for Outstanding Young Teacher of Ministry of Education, China.

REFERENCES

Andricevic, R., and Cvetkovic, V., 1998, Relative dispersion for solute flux in aquifer: J. Fluid Mech., v. 361, p. 145–174.

Bellin, A., and Rinaldo, A., 1995, Analytical solutions for transport of linearly adsorbing solutes in heterogeneous formations: Water Resour. Res., v. 31, no. 6, p. 1505–1511.

Bellin, A., Rinaldo, A., Bosma, W. J. P., van der Zee, S. E. A. T. M., and Rubin, Y., 1993, Linear equilibrium adsorbing solute transport in physically and chemically heterogeneous porous formations, 1, Analytical solutions: Water Resour. Res., v. 29, no.12, p. 4019–4030.

Bellin, A., Rubin, Y., and Rinaldo, A., 1994, Eulerian–Lagrangian approach for modeling of flow and transport in heterogeneous geological formations: Water Resour. Res., v. 30, no. 11, p. 2913–2925.

Bosma, W. J. P., Bellin, A., van der Zee, S. E. A. T. M., and Rinaldo, A., 1993, Linear equilibrium adsorbing solute transport in physically and chemically heterogeneous porous formations, 2, Numerical results: Water Resour. Res., v. 29, no. 12, p. 4031–4043.

Brusseau, M. L., 1994, Transport of reactive contaminants in porous media, Review of Field Experiment, *in* Dracos, T. H., and Stauffer, F., eds., Transport and reactive processes in aquifers: Balkema, Rotterdam, The Netherlands, p. 277–281.

Cushman, J. H., 1997, The physics of fluids in hierarchical porous media: Angstroms to miles: Kluwer Academic, Norwell, MA, 467 p.

Cvetkovic, V., Cheng, H., and Wen, X.-H., 1996, Analysis of nonlinear effects on tracer migration in heterogeneous aquifers using Lagrangian travel time statistics: Water Resour. Res., v. 32, no. 6, p. 1671–1681.

Dagan, G., 1982, Stochastic modeling of groundwater flow by unconditional and conditional probabilities, 2, The solute transport: Water Resour. Res., v. 18, no. 4, p. 835–848.

Dagan, G., 1984, Solute transport in heterogeneous porous formations: J. Fluid Mech., v. 145, p. 151–177.

Dagan G., 1989, Flow and transport in porous formations: Springer, Berlin, 465 p.

Deng, F.-W., Cushman, J. H., and Delleur, J. W., 1993, A fast fourier transform stochastic analysis of the contaminant transport problem: Water Resour. Res., v. 29, no. 9, p. 3241–3247.

Destouni, G., and Cvetkovic, V., 1991, Field scale mass arrival of sorptive solute into the groundwater: Water Resour. Res., v. 27, no. 6, p. 1315–1325.

Gelhar, L. W., 1986, Stochastic subsurface hydrology from theory to applications, Water Resour. Res., v. 22, no. 9, p. 135S–145S.

Gelhar, L. W., and Axness, C. L., 1983, Three-dimensional stochastic analysis of macrodispersion in aquifers: Water Resour. Res., v. 19, no.1, p. 161–180.

Hu, B. X., Deng, F.-W., and Cushman, J. H., 1995, Nonlocal reactive transport with physical and chemical heterogeneity: Linear nonequilibrium sorption with random K_d: Water Resour. Res., v. 31, no. 9, p. 2239–2252.

Naff, R. L., 1990, On the nature of the dispersive flux in saturated heterogeneous porous media: Water Resour. Res., v. 26, no. 5, p. 1013–1026.

Neuman, S. P., and Zhang, Y.-K., 1990, A quasi-linear theory of non-Fickian and Fickian subsurface dispersion, 1, Theoretical analysis with application to isotropic media: Water Resour. Res., v. 26, no. 5, p. 887–902.

Shirley, C., Pohlmann, K., and Andricevic, R., 1997, Three-dimensional mapping of equiprobable hydrostratigraphic units at the Frenchman Flat corrective action unit: Nevada Test Site, Desert Research Institute Pub. No. 45142, DOE/NV/11508-20.

Valocchi, A. J., 1989, Spatial moment analysis of the transport of kinetically adsorbing solutes through stratified aquifers: Water Resour. Res., v. 25, no. 2, p. 273–279.

Winter, C. L., Newman, C. M., and Neuman, S. P., 1984, A perturbation expansion for diffusion in a random velocity field: SIMJ J. Appl. Math., v. 44, no. 2, p. 411–424.

Wu, J., Hu, B. X., and Zhang, D., 2003, Solute transport in nonstationary conductivity fields with complex initial and boundary conditions: J. Hydrol., v. 275, no. 3/4, p. 208–228.

Wu, J., Hu, B. X., and Zhang, D., in press, A three-dimensional numerical method of moments for groundwater flow and solute transport in a nonstationary conductivity field: Adv. Water Res. v. 26, no. 11, p. 1149–1169.

Zhang, D., 2002, Stochastic methods for flow in porous media: Coping with uncertainties: Academic Press, San Diego, CA, 368 p.

Zhang, D., and Winter, C. L., 1999, Moment equation approach to single phase fluid flow in heterogeneous reservoirs: SPEJ Soc. Pet. Eng. J., v. 4, no. 2, p. 118–127.

Zhang, D., Andricevic, R., Sun, A.Y., Hu, B.X., and He, G., 2000, Solute flux approach to transport through spatially nonstationary flow in porous media: Water Resour. Res., v. 36, no. 8, p. 2107–2120.

Zyvoloski, G. A., Robinson, B. A., Birdsell, K. H., Gable, C. W., Czarnecki, J., Bower, K. M., and Faunt, C., 1997, Saturated Zone Radionuclide Transport Model, Yucca Mountain, Nevada: Los Alamos National Laboratory YMP Milestone SP25CM3.