

## Solute flux approach to transport through spatially nonstationary flow in porous media

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**Abstract.** A theoretical framework for solute flux through spatially nonstationary flows in porous media is presented. The flow nonstationarity may stem from medium nonstationarity (e.g., the presence of distinct geological layers, zones, or facies), finite domain boundaries, and/or fluid pumping and injecting. This work provides an approach for studying solute transport in multiscale media, where random heterogeneities exist at some small scale while deterministic geological structures and patterns can be prescribed at some larger scale. In such a flow field the solute flux depends on solute travel time and transverse displacement at a fixed control plane. The solute flux statistics (mean and variance) are derived using the Lagrangian framework and are expressed in terms of the probability density functions (PDFs) of the particle travel time and transverse displacement. These PDFs are given with the statistical moments derived based on nonstationary Eulerian velocity moments. The general approach is illustrated with some examples of conservative and reactive solute transport in stationary and nonstationary flow fields. It is found based on these examples that medium nonstationarities (or multiscale structures and heterogeneities) have a strong impact on predicting solute flux across a control plane and on the corresponding prediction uncertainty. In particular, the behavior of solute flux moments strongly depends on the configuration of nonstationary medium features and the source dimension and location. The developed nonstationary approach may result in non-Gaussian (multiple modal) yet realistic behaviors for solute flux moments in the presence of flow nonstationarities, while these non-Gaussian behaviors may not be reproduced with a traditional stationary approach.

### 1. Introduction

Predicting the migration of contaminants in subsurface flows is a major conceptual and practical challenge. The subsurface flow consists of tortuous and unpredictable flow pathways that result from natural geologic heterogeneity. As a consequence, the contaminant concentration is a random field that can be described only in the statistical sense.

Since geologic media are heterogeneous and the medium heterogeneity generally cannot be described deterministically, it becomes quite common to treat medium properties as spatial random variables. That is, they are unpredictable deterministically and have to be described in statistical terms. In turn, subsurface flow and transport are treated as stochastic processes. Most efforts in studying subsurface contaminant transport in random porous media have been focused on quantifying the expected concentration and the associated uncertainty [e.g., Gelhar and Axness, 1983; Dagan, 1984, 1989; Winter *et al.*, 1984; Neuman, 1993; Graham and McLaughlin, 1989; Cushman and Ginn, 1993; Kapoor and Gelhar, 1994; Zhang and Neuman, 1995]. In most of the previous studies, which were based on either Eulerian or Lagrangian theories, the flow field is com-

monly assumed to be spatially stationary. Recently, Indelman and Rubin [1996] presented a Lagrangian theory for solute transport in nonstationary velocity fields and applied it to the case of transport in media displaying a linear trend in the mean log hydraulic conductivity field. Flow nonstationarity caused by this special case of medium nonstationarity has been extensively studied in the literature [e.g., Rubin and Seong, 1994; Indelman and Rubin, 1995; Li and McLaughlin, 1995; Zhang, 1998].

An alternative representation to concentration is in terms of solute flux, defined as mass of solute per unit time and unit area. The solute flux is related to the flux-averaged concentration by dividing the former by the groundwater flux [Kreft and Zuber, 1978; Dagan *et al.*, 1992]. Current regulatory standards for the subsurface environment, especially those set in terms of travel time, make the solute flux an appealing framework for predicting subsurface contaminant transport. The solute flux integrated over the control plane placed perpendicular to the mean flow was considered as a prime quantity of interest in many previous studies [Dagan and Nguyen, 1989; Cvetkovic *et al.*, 1992; Andricevic and Cvetkovic, 1996; Selroos, 1997]. In these studies the flow field was also assumed to be spatially stationary and temporally steady, and the total solute flux crossing the control plane was considered at the fixed frame of reference (absolute dispersion). Recently, Andricevic and Cvetkovic [1998] reported the solute flux as a function of travel time and transverse displacement in the relative dispersion framework by removing the plume meandering.

For most field applications of the developed theories the assumption of spatially stationary flow is often violated. The

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geologic media are usually composed of different layers and classes of materials with finite boundaries that exhibit different hydraulic properties. Heterogeneity of these different layers or classes creates, in turn, the spatially nonstationary flow conditions. These nonstationary cases (or multiscale structures), which are the reality, were tackled only through extensive numerical simulations. In the subsurface environment the spatial nonstationarity can result not only from the presence of medium nonstationarity (e.g., geologic layers, zones, and facies) but also from fluid pumping and injecting, finite boundaries, and conditioning on measurements.

In this paper a theoretical framework for solute flux through spatially nonstationary flows in porous media is presented. The solute flux depends on the solute travel time and transverse displacement at a fixed control plane. The solute flux statistics (mean and variance) will be derived using a Lagrangian framework and will be expressed in terms of the probability density functions (PDFs) of particle travel time and transverse displacement. These PDFs will be evaluated through the first two moments of travel time and transverse displacement and the assumed distributional form. The latter moments will be obtained from the Eulerian velocity moments. The general approach will be illustrated with some examples of conservative and reactive solute transport in stationary and nonstationary flow fields. Our approach is different from that of *Indelman and Rubin* [1996] in the following aspects: (1) We present a solute flux approach in terms of statistic moments of travel time and transverse displacement, while they derived a resident concentration theory in terms of particle displacement moments, and (2) our expressions are for the general case of nonstationary flow, while theirs are limited to the special case of unidirectional mean flows.

In section 2 the solute transport problem is formulated in a Lagrangian formulation; in section 3 the solute flux statistics are given in terms of the particle travel time and transverse displacement PDFs. In section 4 the explicit expressions for the particle PDFs are given for both unbounded and bounded domains, and the statistical moments of travel time and transverse displacement are expressed as functions of the nonstationary velocity moments. Section 5 illustrates this approach with some examples, and section 6 summarizes this study and discusses the two major assumptions invoked in this paper.

## 2. Problem Formulation

We consider incompressible groundwater flow that takes place through a heterogeneous aquifer of spatially variable hydraulic conductivity  $K(\mathbf{x})$ , where  $\mathbf{x}(x, y, z)$  is a Cartesian coordinate vector. Groundwater seepage velocity  $\mathbf{V}(\mathbf{x})$  satisfies the continuity equation,  $\nabla \cdot (n\mathbf{V}) = 0$ , where  $n$  is the effective porosity. It is considered to be spatially nonstationary because of the bounded domain, sources/sinks, or presence of medium nonstationarity. The velocity is related to the hydraulic conductivity and to the hydraulic head  $h$  through Darcy's law  $\mathbf{V} = -(K/n)\nabla h$ .

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 particle of mass  $\rho_0\Delta\mathbf{a}$  is advected by the random spatially nonstationary groundwater velocity field  $\mathbf{V}$ . The total advected solute mass is

$M = \int_{A_0} \rho_0 d\mathbf{a}$ . If the solute mass is uniformly distributed over  $A_0$ , then  $\rho_0 = M/A_0 = \text{const}$ . 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, through which the solute mass flux is to be predicted or measured; it is referred to as the control plane (CP).

The Lagrangian representation of a marked fluid particle originating from  $\mathbf{x} = \mathbf{a}$  is based on its trajectory  $\mathbf{x} = \mathbf{X}(t; \mathbf{a})$ , which satisfies the kinematic equation

$$d\mathbf{X}/dt = \mathbf{V}[\mathbf{X}(t; \mathbf{a})], \quad (1)$$

where  $\mathbf{V}[\mathbf{X}(t; \mathbf{a})]$  relates the Lagrangian to the Eulerian velocity field. The alternative Lagrangian representation for the solute flux is based on the travel time and follows from

$$t = \tau(x; \mathbf{a}) \quad (2a)$$

which is a solution of

$$x - X_1(t; \mathbf{a}) = 0, \quad (2b)$$

$$\eta(x; \mathbf{a}) = X_2(\tau; \mathbf{a}), \quad \zeta(x; \mathbf{a}) = X_3(\tau; \mathbf{a}). \quad (2c)$$

The function  $\tau(x; \mathbf{a})$  is the travel (residence) time of the advecting fluid particle from  $\mathbf{a}$  to the control plane at  $x$ . Similarly,  $y = \eta(x; \mathbf{a})$  and  $z = \zeta(x; \mathbf{a})$  are the equations of a streamline passing through  $\mathbf{x} = \mathbf{a}$ . These random functions can be related to the velocity field through

$$\frac{d\tau}{dx} = \frac{1}{V_1(x, \eta, \zeta)}, \quad \frac{d\eta}{dx} = \frac{V_2(x, \eta, \zeta)}{V_1(x, \eta, \zeta)}, \quad (3)$$

$$\frac{d\zeta}{dx} = \frac{V_3(x, \eta, \zeta)}{V_1(x, \eta, \zeta)},$$

and the joint PDF for  $\tau$ ,  $\eta$ , and  $\zeta$  quantifies the three-dimensional spreading (transport) of a single particle. In (2) and (3),  $X_i$  and  $V_i$  ( $i = 1, 2, 3$ ) are the components of  $\mathbf{X}$  and  $\mathbf{V}$ , respectively.

## 3. Solute Mass Flux

General mass balance equations for solute undergoing mass transfer reactions are

$$\frac{\partial C}{\partial t} + \mathbf{V} \cdot \nabla C = -\frac{\partial N}{\partial t}, \quad \frac{\partial N}{\partial t} = f(C, N), \quad (4)$$

where local dispersion is neglected. In (4),  $C$  is the mobile and  $N$  is the immobile solute concentration, respectively. In the following we restrict our discussion to linear mass transfer reactions. *Cvetkovic and Dagan* [1994] showed how solute advection along random trajectories can be coupled with the linear reactions yielding the solution in terms of a time retention function  $\gamma(t, \tau)$ , which is available in analytical forms for a wide range of linear solute mass transfer processes.

Integrating the solute flux for a single particle,  $\Delta q \equiv \rho_0(\mathbf{a}) d\mathbf{a} \Gamma(t, \tau) \delta(\mathbf{y} - \boldsymbol{\eta})$ , where  $\boldsymbol{\eta} \equiv \boldsymbol{\eta}(\eta, \zeta)$ , 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 the CP at  $x$  as

$$q(t, \mathbf{y}; x, A) = \frac{1}{A} \int_{A_0} \int_A \rho_0(\mathbf{a}) \Gamma(t, \tau) \delta(\mathbf{y}' - \boldsymbol{\eta}) d\mathbf{y}' d\mathbf{a}, \quad (5)$$

where

$$\Gamma(t, \tau) \equiv \int_0^t \phi(t - t') \gamma(t', \tau) dt' \quad (6)$$

and  $\phi(t)[T^{-1}]$  is the injection rate. The time retention function  $\gamma(t, \tau)$  is the solution for a solute pulse of the advection-reaction system (4), transformed onto an advection flow path. Note that the concentration  $C$  obtained from (4) and the solute flux for a single particle,  $\Delta q$ , are related as  $\Delta q = CV_x(x, \eta, \zeta)$ . For instantaneous release,  $\phi \equiv \delta(t)$ ; for nonreactive solute,  $\gamma \equiv \delta(t - \tau)$ . For instantaneous release of nonreactive solute, (6) yields  $\Gamma = \delta(t - \tau)$ . For solutes undergoing a sorption-desorption reaction controlled by first-order kinetics, the time retention function is [Lassey, 1988; Cvetkovic and Dagan, 1994; Andricevic and Cvetkovic, 1998]

$$\begin{aligned} \gamma(t, \tau) = & \exp[-(\alpha K_d + k_0)t] \delta(t - \tau) + \alpha^2 K_d \tau \\ & \cdot \exp(-\alpha K_d \tau - \alpha t + \alpha \tau - k_0 t) \\ & \cdot \bar{I}_1[\alpha^2 K_d \tau(t - \tau)] H(t - \tau), \end{aligned} \quad (7)$$

where  $\bar{I}_1(z) = I_1(2z^{1/2})/z^{1/2}$  with  $I_1$  being the modified Bessel function of the first kind of order one,  $\alpha$  is the mass transfer rate,  $K_d$  is the distribution coefficient once equilibrium is reached for reversible mass transfer,  $H(t - \tau)$  is the Heaviside step function, and  $k_0$  is the irreversible mass transfer coefficient (accounting for decay or degradation in both mobile and immobile phases). For  $\alpha \rightarrow \infty$ , reversible mass transfer is under equilibrium conditions, and one has  $\gamma = \exp(-k_0 t) \delta[t - (1 + K_d)\tau]$ .

### 3.1. Moments of Solute Flux

In (5) both  $\tau$  and  $\eta$  are random variables and are functions of the underlying random velocity field. The expected value of  $q$  in (5) can be expressed as

$$\begin{aligned} \langle q(t, \mathbf{x}; A) \rangle = & \frac{1}{A} \int_{A_0} \int_A \int_0^\infty \rho_0(\mathbf{a}) \Gamma(t, \tau) \delta(\mathbf{y}' - \eta) \\ & \cdot f_1[\tau(x, \mathbf{a}), \eta(x, \mathbf{a})] d\eta d\tau d\mathbf{y}' d\mathbf{a}, \end{aligned} \quad (8)$$

where  $\mathbf{x} \equiv \mathbf{x}(x, \mathbf{y})$  and  $f_1[\tau(x, \mathbf{a}), \eta(x, \mathbf{a})]$  denotes the joint PDF of travel time  $\tau$  for a particle starting from  $\mathbf{a}$  to reach  $x$  and the corresponding transverse displacement  $\eta$ . From now on, we consider the case of point sampling (i.e.,  $A \rightarrow 0$ ),

$$\begin{aligned} \langle q(t, \mathbf{x}) \rangle = & \int_{A_0} \int_0^\infty \rho_0(\mathbf{a}) \Gamma(t, \tau) \\ & \cdot f_1[\tau(x, \mathbf{a}), \eta(x, \mathbf{a}) = \mathbf{y}] d\tau d\mathbf{a}. \end{aligned} \quad (9)$$

The variance of the solute flux for the point sampling is evaluated as

$$\sigma_q^2(t, \mathbf{x}) = \langle q^2 \rangle - \langle q \rangle^2, \quad (10)$$

where

$$\langle q^2(t, \mathbf{x}) \rangle = \int_{A_0} \int_{A_0} \rho_0(\mathbf{a}) \rho_0(\mathbf{b}) F(t, \mathbf{y}; x, \mathbf{a}, \mathbf{b}) d\mathbf{a} d\mathbf{b} \quad (11)$$

with

$$\begin{aligned} F(t, \mathbf{y}; x, \mathbf{a}, \mathbf{b}) = & \int_0^\infty \int_0^\infty \Gamma(t, \tau_1) \Gamma(t, \tau_2) f_2[\tau_1(x; \mathbf{a}), \\ & \eta_1(x; \mathbf{a}) = \mathbf{y}; \tau_2(x; \mathbf{b}), \eta_2(x; \mathbf{b}) = \mathbf{y}] d\tau_1 d\tau_2, \end{aligned} \quad (12)$$

For the special case of nonreactive solute pulse,

$$\langle q(t, \mathbf{x}) \rangle = \int_{A_0} \rho_0(\mathbf{a}) f_1[\tau(x, \mathbf{a}) = t, \eta(x, \mathbf{a}) = \mathbf{y}] d\mathbf{a}, \quad (13)$$

$$\begin{aligned} \langle q^2(t, \mathbf{x}) \rangle = & \int_{A_0} \int_{A_0} \rho_0(\mathbf{a}) \rho_0(\mathbf{b}) f_2[\tau_1(x; \mathbf{a}) = t, \\ & \eta_1(x; \mathbf{a}) = \mathbf{y}; \tau_2(x; \mathbf{b}) = t, \eta_2(x; \mathbf{b}) = \mathbf{y}] d\mathbf{a} d\mathbf{b}. \end{aligned} \quad (14)$$

Here  $f_2[\tau_1(x; \mathbf{a}), \eta_1(x; \mathbf{a}); \tau_2(x; \mathbf{b}), \eta_2(x; \mathbf{b})]$  is the two-particle joint PDF of travel time and transverse displacement. For the special case of stationary flow the PDFs do not depend on the absolute locations of the starting point  $\mathbf{a}(a_x, a_y, a_z)$  and the CP  $x$  but depend on their relative distance. For example, in that case the one particle joint PDF reads as  $f_1[\tau(x - a_x, \mathbf{0}) = t, \eta(x - a_x, \mathbf{0}) = \mathbf{y}]$ . In stationary flows,  $\tau(x; \mathbf{a})$  and  $\eta(x; \mathbf{a})$  are uncorrelated, at least up to second-order in the variance of log hydraulic conductivity [Dagan et al., 1992], and thus  $f_1[\tau, \eta] = f_1[\tau] f_1[\eta]$ . This has been assumed also for the two-particle joint PDFs in the literature [e.g., Andricevic and Cvetkovic, 1998], that is,  $f_2[\tau_1(x; \mathbf{a}), \eta_1(x; \mathbf{a}); \tau_2(x; \mathbf{b}), \eta_2(x; \mathbf{b})] = f_2[\tau_1(x; \mathbf{a}), \tau_2(x; \mathbf{b})] f_2[\eta_1(x; \mathbf{a}), \eta_2(x; \mathbf{b})]$ . However, as shown in section 5.1, this assumption may not hold for two-particle joint PDFs.

### 3.2. Moments of Total Solute Flux

The solute discharge is another quantity of interest defined as the total solute mass flux over the entire control plane (CP) at  $x$ , rather than for the point  $\mathbf{x}$ ,

$$Q(t, x) = \int_{A_0} \int_{CP} \rho_0(\mathbf{a}) \Gamma(t, \tau) \delta(\mathbf{y} - \eta) d\mathbf{a} d\mathbf{y}, \quad (15)$$

where  $\mathbf{y}$  is a point in the CP. Its mean and variance are given as

$$\langle Q(t, x) \rangle = \int_{A_0} \int_0^\infty \rho_0(\mathbf{a}) \Gamma(t, \tau) f_1[\tau(x, \mathbf{a})] d\tau d\mathbf{a}, \quad (16)$$

$$\sigma_Q^2(t, x) = \langle Q^2 \rangle - \langle Q \rangle^2, \quad (17)$$

$$\langle Q^2(t, x) \rangle = \int_{A_0} \int_{A_0} \rho_0(\mathbf{a}) \rho_0(\mathbf{b}) F(t; x, \mathbf{a}, \mathbf{b}) d\mathbf{a} d\mathbf{b}, \quad (18)$$

with

$$\begin{aligned} F(t; x, \mathbf{a}, \mathbf{b}) = & \int_0^\infty \int_0^\infty \\ & \cdot \Gamma(t, \tau_1) \Gamma(t, \tau_2) f_2[\tau_1(x; \mathbf{a}); \tau_2(x; \mathbf{b})] d\tau_1 d\tau_2. \end{aligned} \quad (19)$$

Here  $f_1[\tau(x, \mathbf{a})]$  is the marginal PDF of  $f_1[\tau(x, \mathbf{a}), \eta(x, \mathbf{a})]$ , and  $f_2[\tau_1(x; \mathbf{a}); \tau_2(x; \mathbf{b})]$  is the marginal PDF of  $f_2[\tau_1(x; \mathbf{a}), \eta_1(x; \mathbf{a}); \tau_2(x; \mathbf{b}), \eta_2(x; \mathbf{b})]$ .

For the case of nonreactive solute pulse,

$$\langle Q(t, x) \rangle = \int_{A_0} \rho_0(\mathbf{a}) f_1[\tau(x, \mathbf{a}) = t] d\mathbf{a}, \quad (20)$$

$$\langle Q^2(t, x) \rangle = \int_{A_0} \int_{A_0} \rho_0(\mathbf{a}) \rho_0(\mathbf{b}) \cdot f_2[\tau_1(x; \mathbf{a}) = t; \tau_2(x; \mathbf{b}) = t] d\mathbf{a} d\mathbf{b}. \quad (21)$$

#### 4. Joint Probability Density Functions

It is seen from section 3 that in order to evaluate the statistical moments of solute flux, the knowledge of the one- and two-particle PDFs  $f_1$  and  $f_2$  or an infinite number of statistical moments, is needed. Our approach to this Lagrangian closure problem is to evaluate a finite number of statistical moments and assume certain shapes for  $f_1$  and  $f_2$ .

It is reasonable to approximate travel time  $\tau$  with a lognormal distribution and transverse displacement  $\eta$  as a normal distribution [Bellin et al., 1994; Cvetkovic et al., 1996]. With this Lagrangian closure the evaluation of PDFs becomes that of the first two moments of  $\tau$  and  $\eta$  and that of their joint moments.

The joint moment between the travel time and transverse displacements  $\sigma_{\tau\eta} \equiv \langle \tau\eta \rangle - \langle \tau \rangle \langle \eta \rangle$  was assumed to be zero for statistically stationary flows [Dagan et al., 1992]. However, for nonstationary velocity field it is nonzero and will be evaluated below. In the following we wish to compute the first few moments of the PDFs  $f_1(\tau_1, \eta_1)$  and  $f_2(\tau_1, \eta_1; \tau_2, \eta_2)$ .

The key elements in evaluating the mean solute flux for spatially nonstationary velocity fields are the first two moments of the travel time and transverse displacements. In the spatially stationary flow the first moments are trivial, while the second moments are derived analytically up to first order as functions of the stationary velocity covariances [Rubin, 1990; Rubin and Dagan, 1992; Zhang and Neuman, 1992]. For the case of a spatially nonstationary velocity field the first two moments of travel time and transverse displacement are much more complex. In section 4.1 we will derive these two moments as functions of nonstationary velocity moments, which are, in turn, obtained with the semianalytical flow approach of Zhang [1998] and Zhang and Winter [1999]. In section 4.2 we will utilize these moments to construct the PDFs of travel time and transverse displacement. With these PDFs the expected value and the standard deviation of solute flux can be evaluated.

##### 4.1. Travel Time and Transverse Displacement Moments

Since our examples, for illustrative purposes, will be two-dimensional (2-D), we will focus on our developments in 2-D form. The travel time  $\tau(L; \mathbf{a})$ , the time required for a particle originated at  $\mathbf{a}$  to cross the line  $x = L$  in two-dimensions, can be expressed from (3) as

$$\tau(L; \mathbf{a}) = \int_{a_x}^L \frac{dx}{V_1[x, \eta(x; \mathbf{a})]}, \quad (22)$$

where  $\mathbf{a} = (a_x, a_y)^T$  with  $T$  indicating transpose. Since the Eulerian velocity  $\mathbf{V}(x, y)$  is a random variable, so are the Lagrangian velocity  $\mathbf{V}[x, \eta(x; \mathbf{a})]$ , the travel time  $\tau(L; \mathbf{a})$ , and the transverse displacement  $\eta(x; \mathbf{a})$ . We decompose the Eulerian velocity as  $\mathbf{V}(\mathbf{x}) = \mathbf{U}(\mathbf{x}) + \mathbf{u}(\mathbf{x})$ , where  $\mathbf{x} = (x, y)^T$ ,  $\mathbf{U}$  is the ensemble mean velocity, and  $\mathbf{u}$  is a zero-mean velocity fluctuation. For the Lagrangian velocity  $\mathbf{V}[x, \eta(x; \mathbf{a})]$  both the particle transverse position  $\eta$  and the velocity  $\mathbf{V}$

at this location are random. We may expand the Lagrangian velocity around its mean path  $[x, \langle \eta(x; \mathbf{a}) \rangle]$  in a Taylor series,

$$V_1(x, \eta) = U_1(x, \langle \eta \rangle) + u_1(x, \langle \eta \rangle) + \eta' \left. \frac{\partial U_1(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} + \cdots, \quad (23)$$

where  $\eta' = \eta - \langle \eta \rangle$  with  $\langle \eta' \rangle \equiv 0$ . It is important to mention that in the previous studies, where flow is assumed to be spatially stationary, the mean velocity  $U_1$  is constant so that only the first two terms on the right-hand side of (23) exist. For nonstationary flow the derivative of  $U_1$  is generally nonzero. We may also decompose  $\tau$  into its mean  $\langle \tau \rangle$  and fluctuation  $\tau'$ . With (23), (22) can be rewritten as

$$\begin{aligned} \tau(L; \mathbf{a}) &= \int_{a_x}^L \left[ U_1(x, \langle \eta \rangle) + u_1(x, \langle \eta \rangle) \right. \\ &\quad \left. + \eta' \left. \frac{\partial U_1(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} + \cdots \right]^{-1} dx \\ &= \int_{a_x}^L \frac{1}{U_1(x, \langle \eta \rangle)} \left[ 1 - \frac{u_1(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} \right. \\ &\quad \left. - \frac{\eta'}{U_1(x, \langle \eta \rangle)} \left. \frac{\partial U_1(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} + \cdots \right] dx. \end{aligned} \quad (24)$$

Hence we have, to first-order,

$$\langle \tau(L; \mathbf{a}) \rangle = \int_{a_x}^L \frac{dx}{U_1(x, \langle \eta \rangle)}, \quad (25)$$

$$\begin{aligned} \tau'(L; \mathbf{a}) &= - \int_{a_x}^L \frac{1}{U_1^2(x, \langle \eta \rangle)} [u_1(x, \langle \eta \rangle) \\ &\quad + b_1(x, \langle \eta \rangle) \eta'] dx, \end{aligned} \quad (26)$$

where  $\eta = \eta(x; \mathbf{a})$  and  $b_1(x, \langle \eta \rangle) = \{[\partial U_1(x, y)]/\partial y\}|_{y=\langle \eta \rangle}$ . These expressions are derived up to first order and therefore require the coefficient of variation of velocity to be (formally, much) smaller than 1. This condition may be satisfied for many practical subsurface flows where the variance of log-transformed permeability is moderately large. With (26) we obtain the variance for the travel time as

$$\begin{aligned} \sigma_{\tau}^2(L; \mathbf{a}) &= \int_{a_x}^L \int_{a_x}^L \frac{dx_1 dx_2}{U_1^2(x_1, \langle \eta_1 \rangle) U_1^2(x_2, \langle \eta_2 \rangle)} \\ &\quad \cdot [\langle u_1(x_1, \langle \eta_1 \rangle) u_1(x_2, \langle \eta_2 \rangle) \rangle + 2b_1(x_2, \langle \eta_2 \rangle) \\ &\quad \cdot \langle u_1(x_1, \langle \eta_1 \rangle) \eta_2' \rangle + b_1(x_1, \langle \eta_1 \rangle) b_1(x_2, \langle \eta_2 \rangle) \langle \eta_1' \eta_2' \rangle], \end{aligned} \quad (27)$$

where  $\eta_1 = \eta(x_1; \mathbf{a})$  and  $\eta_2 = \eta(x_2; \mathbf{a})$ . The two-particle joint moment  $\sigma_{\tau_1 \tau_2}$  can be written similarly as

$$\begin{aligned} \sigma_{\tau_1\tau_2}(L, \mathbf{a}; L, \mathbf{b}) &= \int_{a_x}^L \int_{b_x}^L \frac{dx_1 dx_2}{U_1^2(x_1, \langle \eta_1 \rangle) U_1^2(x_2, \langle \eta_2 \rangle)} \\ &\cdot [\langle u_1(x_1, \langle \eta_1 \rangle) u_1(x_2, \langle \eta_2 \rangle) \rangle + b_1(x_1, \langle \eta_1 \rangle) \\ &\cdot \langle u_1(x_2, \langle \eta_2 \rangle) \eta'_1 \rangle + b_1(x_2, \langle \eta_2 \rangle) \langle u_1(x_1, \langle \eta_1 \rangle) \eta'_2 \rangle \\ &+ b_1(x_1, \langle \eta_1 \rangle) b_1(x_2, \langle \eta_2 \rangle) \langle \eta'_1 \eta'_2 \rangle], \end{aligned} \quad (28)$$

where  $\eta_1 = \eta(x_1; \mathbf{a})$  and  $\eta_2 = \eta(x_2; \mathbf{b})$ . It is seen that (28) reduces to (27) by setting  $\mathbf{b} = \mathbf{a}$ .

Now we look at how to derive the statistical moments for  $\eta$ , which can be rewritten as

$$\eta(L; \mathbf{a}) = \int_{a_x}^L \frac{V_2(x, \eta)}{V_1(x, \eta)} dx. \quad (29)$$

Similar to (23), we have

$$\begin{aligned} V_2(x, \eta) &= U_2(x, \langle \eta \rangle) + u_2(x, \langle \eta \rangle) \\ &+ \eta' \left. \frac{\partial U_2(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} + \dots \end{aligned} \quad (30)$$

Therefore, together with (23) and (30), we may rewrite (3) as

$$\begin{aligned} \frac{d\eta(x; \mathbf{a})}{dx} &= \frac{1}{U_1(x, \langle \eta \rangle)} \left[ U_2(x, \langle \eta \rangle) + u_2(x, \langle \eta \rangle) \right. \\ &- \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle) + \eta' \left. \frac{\partial U_2(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} \\ &- \eta' \left. \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} \frac{\partial U_1(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} + \dots \left. \right]. \end{aligned} \quad (31)$$

Therefore, to first order,

$$\frac{d\langle \eta(x; \mathbf{a}) \rangle}{dx} = \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} \quad (32)$$

$$\begin{aligned} \frac{d\eta'(x; \mathbf{a})}{dx} &= \frac{1}{U_1(x, \langle \eta \rangle)} \left[ u_2(x, \langle \eta \rangle) \right. \\ &- \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle) + \eta' \left. \frac{\partial U_2(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} \\ &- \eta' \left. \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} \frac{\partial U_1(x, \eta)}{\partial \eta} \right|_{\eta=\langle \eta \rangle} \left. \right]. \end{aligned} \quad (33)$$

After some mathematical manipulations (see the appendix), (33) can be rewritten as

$$\begin{aligned} \eta'(L; \mathbf{a}) U_1(L, \langle \eta \rangle) &= \int_{a_x}^L \left[ u_2(x, \langle \eta \rangle) \right. \\ &- \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle) \left. \right] dx. \end{aligned} \quad (34)$$

Therefore, to first order,

$$\langle \eta(L; \mathbf{a}) \rangle = \int_{a_x}^L \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} dx, \quad (35)$$

$$\begin{aligned} \sigma_{\eta}^2(L; \mathbf{a}) &= \frac{1}{U_1^2(L, \langle \eta \rangle)} \int_{a_x}^L \int_{a_x}^L [\langle u_2(x_1, \langle \eta_1 \rangle) u_2(x_2, \langle \eta_2 \rangle) \rangle \\ &+ a_1(x_1, \langle \eta_1 \rangle) a_1(x_2, \langle \eta_2 \rangle) \\ &\cdot \langle u_1(x_1, \langle \eta_1 \rangle) u_1(x_2, \langle \eta_2 \rangle) \rangle - 2a_1(x_1, \langle \eta_1 \rangle) \\ &\cdot \langle u_1(x_1, \langle \eta_1 \rangle) u_2(x_2, \langle \eta_2 \rangle) \rangle] dx_1 dx_2, \end{aligned} \quad (36)$$

where  $a_1(x_1, \langle \eta_1 \rangle) = [U_2(x_1, \langle \eta_1 \rangle)]/[U_1(x_1, \langle \eta_1 \rangle)]$ . We can write an expression for  $\sigma_{\eta_1\eta_2}(L, \mathbf{a}; L, \mathbf{b})$  similarly.

With (34) we may also give other terms required to evaluate  $\sigma_{\tau}^2$  and  $\sigma_{\tau_1\tau_2}$  in (27) and (28), respectively,

$$\begin{aligned} &\langle u_1(x_1, \langle \eta_1(x_1; \mathbf{a}) \rangle) \eta'_2(x_2; \mathbf{b}) \rangle \\ &= \frac{1}{U_1(x_2, \langle \eta_2 \rangle)} \int_{b_x}^{x_2} [\langle u_1(x_1, \langle \eta_1 \rangle) u_2(x_2, \langle \eta_2 \rangle) \rangle \\ &- a_1(x_2, \langle \eta_2 \rangle) \langle u_1(x_1, \langle \eta_1 \rangle) \rangle \\ &\cdot \langle u_1(x_1, \langle \eta_1 \rangle) u_1(x_2, \langle \eta_2 \rangle) \rangle] d\chi, \end{aligned} \quad (37)$$

$$\begin{aligned} \langle \eta'_1(x_1; \mathbf{a}) \eta'_2(x_2; \mathbf{b}) \rangle &= \frac{1}{U_1(x_1, \langle \eta_1 \rangle) U_1(x_2, \langle \eta_2 \rangle)} \int_{a_x}^{x_1} \int_{b_x}^{x_2} \\ &\cdot [\langle u_2(x_1, \langle \eta_1 \rangle) u_2(x_2, \langle \eta_2 \rangle) \rangle \\ &+ a_1(x_1, \langle \eta_1 \rangle) a_1(x_2, \langle \eta_2 \rangle) \\ &\cdot \langle u_1(x_1, \langle \eta_1 \rangle) u_1(x_2, \langle \eta_2 \rangle) \rangle - a_1(x_1, \langle \eta_1 \rangle) \\ &\cdot \langle u_1(x_1, \langle \eta_1 \rangle) u_2(x_2, \langle \eta_2 \rangle) \rangle - a_1(x_2, \langle \eta_2 \rangle) \\ &\cdot \langle u_1(x_2, \langle \eta_2 \rangle) u_2(x_1, \langle \eta_1 \rangle) \rangle] d\chi_1 d\chi_2. \end{aligned} \quad (38)$$

The joint moment  $\langle \tau'_1(x_1; \mathbf{a}) \eta'_2(x_2; \mathbf{b}) \rangle$  can be given as

$$\begin{aligned} &\langle \tau'_1(x_1; \mathbf{a}) \eta'_2(x_2; \mathbf{b}) \rangle \\ &= - \int_{a_x}^{x_1} \frac{1}{U_1^2(x, \langle \eta(x; \mathbf{a}) \rangle)} \\ &\cdot [\langle u_1(x, \langle \eta(x; \mathbf{a}) \rangle) \eta'_2(x_2; \mathbf{b}) \rangle + b_1(x, \langle \eta(x; \mathbf{a}) \rangle) \\ &\langle \eta'_1(x; \mathbf{a}) \eta'_2(x_2; \mathbf{b}) \rangle] d\chi. \end{aligned} \quad (39)$$

For the special cases of uniform mean flow where  $U_i(\mathbf{x}) = \delta_{i1}\mu$ , we have the coefficients  $a_1 = b_1 = b_2 = 0$ ,  $\langle \tau \rangle = (L - a_x)/\mu$ , and  $\langle \eta \rangle = 0$ ; we can significantly simplify the expressions for  $\sigma_{\tau}^2$  and  $\sigma_{\eta}^2$  as

$$\sigma_{\tau}^2(L; \mathbf{a}) = \frac{1}{\mu^4} \int_{a_x}^L \int_{a_x}^L C_{u_{11}}(x_1 - x_2, 0) dx_1 dx_2, \quad (40)$$

$$\sigma_{\eta}^2(L; \mathbf{a}) = \frac{1}{\mu^2} \int_{a_x}^L \int_{a_x}^L C_{u_{22}}(x_1 - x_2, 0) dx_1 dx_2, \quad (41)$$

where  $C_{u_{ij}}(x_1 - x_2, y_1 - y_2) = \langle u_i(x_1, y_1) u_j(x_2, y_2) \rangle$ . These are equivalent to the formulae given by *Dagan et al.* [1992]. Almost all previous studies have focused on this special

case. Another special case is that the mean flow is unidirectional but varies in space, which can be the case of saturated flow with trending permeability in bounded domains. Assuming the mean flow is aligned with the  $x$  direction, for this special case we have

$$\sigma_{\tau}^2(L; \mathbf{a}) = \int_{a_x}^L \int_{a_x}^L \frac{1}{U_1^2(x_1, \langle \eta_1 \rangle) U_1^2(x_2, \langle \eta_2 \rangle)} \cdot C_{u11}(x_1, \langle \eta_1 \rangle; x_2, \langle \eta_2 \rangle) dx_1 dx_2, \quad (42)$$

$$\sigma_{\eta}^2(L; \mathbf{a}) = \int_{a_x}^L \int_{a_x}^L \frac{1}{U_1(x_1, \langle \eta_1 \rangle) U_1(x_2, \langle \eta_2 \rangle)} \cdot C_{u22}(x_1, \langle \eta_1 \rangle; x_2, \langle \eta_2 \rangle) dx_1 dx_2. \quad (43)$$

#### 4.2. Explicit Expressions for PDFs

If  $\tau$  and  $\eta$  obey a lognormal and normal distribution, respectively, their joint PDF for one particle can be expressed as [e.g., *Bras and Rodriguez-Iturbe, 1984*]

$$f_1[\tau(x; \mathbf{a}), \eta(x; \mathbf{a})] = \frac{1}{2\pi\tau\sigma_{\eta}(x; \mathbf{a})\sigma_{\ln \tau}(x; \mathbf{a})\sqrt{1-r^2}} \cdot \exp \left\{ -\frac{1}{2(1-r^2)} \left[ \frac{(\eta - \langle \eta(x; \mathbf{a}) \rangle)^2}{\sigma_{\eta}^2} - 2r \frac{(\eta - \langle \eta(x; \mathbf{a}) \rangle)(\ln \tau - \langle \ln \tau(x; \mathbf{a}) \rangle)}{\sigma_{\eta}(x; \mathbf{a})\sigma_{\ln \tau}(x; \mathbf{a})} + \frac{(\ln \tau - \langle \ln \tau(x; \mathbf{a}) \rangle)^2}{\sigma_{\ln \tau}^2(x; \mathbf{a})} \right] \right\}, \quad (44)$$

where  $\sigma_{\ln \tau}^2(x; \mathbf{a}) = \ln [\sigma_{\tau}^2(x; \mathbf{a}) + \langle \tau(x; \mathbf{a}) \rangle^2] - 2 \ln \langle \tau(x; \mathbf{a}) \rangle$ ,  $\langle \ln \tau(x; \mathbf{a}) \rangle = 2 \ln \langle \tau(x; \mathbf{a}) \rangle - \frac{1}{2} \ln [\sigma_{\tau}^2(x; \mathbf{a}) + \langle \tau(x; \mathbf{a}) \rangle^2]$ , and  $r = \langle \tau'(x; \mathbf{a})\eta'(x; \mathbf{a}) \rangle / [\sigma_{\eta}(x; \mathbf{a})\sigma_{\ln \tau}(x; \mathbf{a})\langle \tau(x; \mathbf{a}) \rangle]$ .

Similarly, the joint two-particle PDF of  $(\tau_1, \eta_1)$  and  $(\tau_2, \eta_2)$  can be expressed as

$$f_2[\tau_1(x; \mathbf{a}), \eta_1(x; \mathbf{a}); \tau_2(x; \mathbf{b}), \eta_2(x; \mathbf{b})] = \frac{1}{(2\pi)^2\tau_1\tau_2|\Sigma|^{1/2}} \exp \left\{ -\frac{1}{2} \mathbf{X}^T \Sigma^{-1} \mathbf{X} \right\}, \quad (45)$$

where  $\mathbf{X} = [(\ln \tau_1 - \langle \ln \tau_1 \rangle), (\eta_1 - \langle \eta_1 \rangle), (\ln \tau_2 - \langle \ln \tau_2 \rangle), (\eta_2 - \langle \eta_2 \rangle)]^T$  and  $\Sigma$  is the covariance matrix given as

$$\Sigma = \begin{pmatrix} \sigma_{\ln \tau_1}^2 & \sigma_{\ln \tau_1 \eta_1} & \sigma_{\ln \tau_1 \ln \tau_2} & \sigma_{\ln \tau_1 \eta_2} \\ \sigma_{\ln \tau_1 \eta_1} & \sigma_{\eta_1}^2 & \sigma_{\ln \tau_2 \eta_1} & \sigma_{\eta_1 \eta_2} \\ \sigma_{\ln \tau_1 \ln \tau_2} & \sigma_{\ln \tau_2 \eta_1} & \sigma_{\ln \tau_2}^2 & \sigma_{\ln \tau_2 \eta_2} \\ \sigma_{\ln \tau_1 \eta_2} & \sigma_{\eta_1 \eta_2} & \sigma_{\ln \tau_2 \eta_2} & \sigma_{\eta_2}^2 \end{pmatrix}. \quad (46)$$

In (46),  $\langle \ln \tau_i \rangle = 2 \ln \langle \tau_i \rangle - \frac{1}{2} \ln [\sigma_{\tau_i}^2 + \langle \tau_i \rangle^2]$ ,  $\sigma_{\ln \tau_i}^2 = \ln [\sigma_{\tau_i}^2 + \langle \tau_i \rangle^2] - 2 \ln \langle \tau_i \rangle$ ,  $\sigma_{\ln \tau_i \eta_j} = \langle \tau'_i \eta'_j \rangle / \langle \tau_i \rangle$ , and  $\sigma_{\ln \tau_i \ln \tau_j} = \ln [\langle \tau_i \rangle \langle \tau_j \rangle + \langle \tau'_i \tau'_j \rangle] - \ln [\langle \tau_i \rangle \langle \tau_j \rangle]$ . Note that  $f_2$  in (45) reduces to  $f_1$  in (44) by retaining only the first two variables in the former and setting  $r = \sigma_{\ln \tau_1 \eta_1} / [\sigma_{\ln \tau_1} \sigma_{\eta_1}]$ . As seen in the above, the various  $\ln \tau$  and  $\eta$  moments required in (44)–(46) can all be expressed with the raw moments of  $\tau$  and  $\eta$ . The required PDFs for evaluating the various solute flux moments in (9)–(11) and (16)–(18), and the required  $\tau$  and  $\eta$  moments for the PDFs, are summarized in Table 1.

In the above PDFs the transverse displacement  $\eta$  can vary

**Table 1.** Required Travel Time and Transverse Displacement PDFs and Moments for Evaluating the Moments of Solute Flux

Quantities	Required PDFs	Required Moments
$\langle Q(t, x) \rangle$	$f_1(\tau)$	$\langle \tau \rangle, \sigma_{\tau}^2$
$\langle Q^2(t, x) \rangle$	$f_2(\tau_1; \tau_2)$	$\langle \tau_i \rangle, \sigma_{\tau_i}^2, \langle \tau'_i \tau'_j \rangle$
$\langle q(t, x, y) \rangle$	$f_1(\tau, \eta)$	$\langle \tau \rangle, \sigma_{\tau}^2, \langle \eta \rangle, \sigma_{\eta}^2, \langle \tau' \eta' \rangle$
$\langle q^2(t, x, y) \rangle$	$f_2(\tau_1, \eta_1; \tau_2, \eta_2)$	$\langle \tau_i \rangle, \sigma_{\tau_i}^2, \langle \eta_i \rangle, \sigma_{\eta_i}^2, \langle \tau'_i \tau'_j \rangle, \langle \tau'_i \eta'_j \rangle, \langle \eta'_i \eta'_j \rangle$

Note that  $i = 1, 2$  and  $j = 1, 2$ .

from  $-\infty$  to  $\infty$ . This condition is clearly not satisfied for bounded domains. In the latter case the PDFs in (44) and (45) can be regarded as fundamental expressions, and the true PDFs may be obtained by the principle of superposition. For example, if a rectangular domain of transverse dimension  $L$  is bounded by two no-flow sides at  $y = y_0$  and  $y = y_L$  such that  $\eta \in [y_0, y_L]$ , after accounting for the boundary conditions the one-particle joint PDF can be given by the principle of superposition [e.g., *Fischer et al., 1979*] as

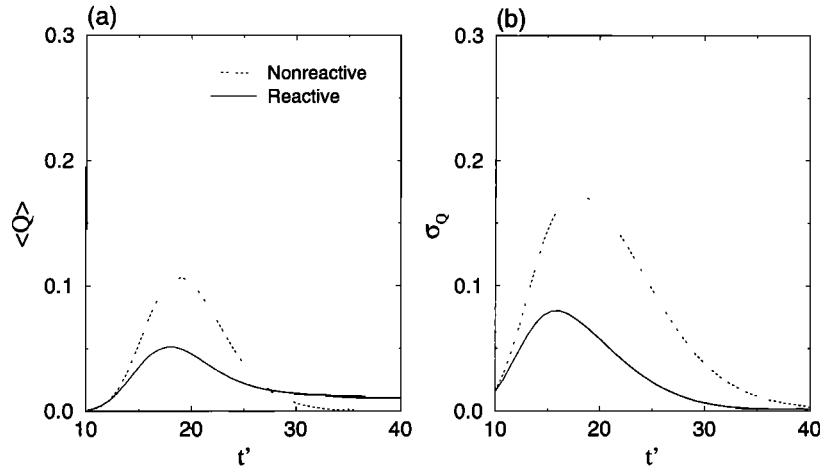
$$f_1^B[\tau(x; \mathbf{a}), \eta(x; \mathbf{b})] = f_1[\tau, \eta] + \sum_{n=0}^{\infty} \{f_1[\tau, 2(y_0 - nL) - \eta] + f_1[\tau, 2(y_L + nL) - \eta]\}, \quad (47)$$

where  $\eta \in [y_0, y_L]$  and  $f_1[\tau, \eta]$  are given by (44). It usually suffices to use only a few terms to achieve convergence. Here the transverse displacement satisfies a truncated normal distribution. The two-particle joint PDF  $f_2^B$  can be constructed similarly for bounded domains.

#### 5. Illustrative Examples

In this section we illustrate our approach through some examples of reactive and nonreactive solute transport in stationary and nonstationary flow fields. Section 5.1 involves a stationary flow field, as a special case of our general approach. The purpose of subsection 5.1 is to compare with literature results and to discuss the validity of a common assumption made for the two-particle joint PDF. In section 5.2 we discuss the effects of flow nonstationarity on the prediction of reactive and nonreactive solute flux and the associated uncertainty.

The spatial nonstationarity in flow may be caused by fluid pumping and injecting, the presence of finite boundaries, and the presence of medium nonstationarity (e.g., distinct geologic layers, zones, and facies). In our examples, flow nonstationarity is due to the combined effects of finite boundaries and the nonstationarity in the log hydraulic conductivity  $Y$  field. The nonstationarity in the  $Y$  field may manifest in two ways: The mean  $\langle Y \rangle$  may vary spatially, and the two-point covariance  $C_Y(\mathbf{x}, \mathbf{x})$  may depend on the actual locations of  $\mathbf{x}$  and  $\mathbf{x}$  rather than only on their separation distance. The latter may be a result of conditioning. For the nonstationary case the statistical moments for the velocity field are obtained with the semianalytical flow approach of *Zhang [1998]* and *Zhang and Winter [1999]*. In that approach, general equations governing the statistical moments of flow quantities are derived by perturbation expansions. Owing to the mathematical complexity caused by the presence of boundaries and medium nonstationarity, these moment equations are solved numerically. Although the semi-



**Figure 1.** (a) Expected value  $\langle Q \rangle$  and (b) standard deviation  $\sigma_Q$  of total solute flux across the control plane at  $x = 20\lambda$  (where  $\lambda$  is the correlation scale of the underlying permeability field) as a function of dimensionless time with and without reaction (stationary flow case).

analytical flow approach can handle the general type of medium nonstationarity, in the following examples we consider the case that the log hydraulic conductivity consists of a non-constant mean and a stationary fluctuation. That is to say, the mean varies spatially and the two-point covariance only depends on the relative distance. Although the semianalytical flow approach admits any covariance function, we consider for simplicity only the exponential covariance for  $Y$  field,

$$C_Y(\mathbf{x} - \mathbf{x}') = \sigma_Y^2 \exp \left\{ - \left[ \frac{(\mathbf{x} - \mathbf{x}')^2}{\lambda_i^2} \right]^{1/2} \right\}, \quad (48)$$

where  $\sigma_Y^2$  is the variance and  $\lambda_i$  is the correlation scale of  $Y$  along the  $x_i$  axis. For  $\lambda_1 = \lambda_2 = \lambda$  the covariance function is isotropic.

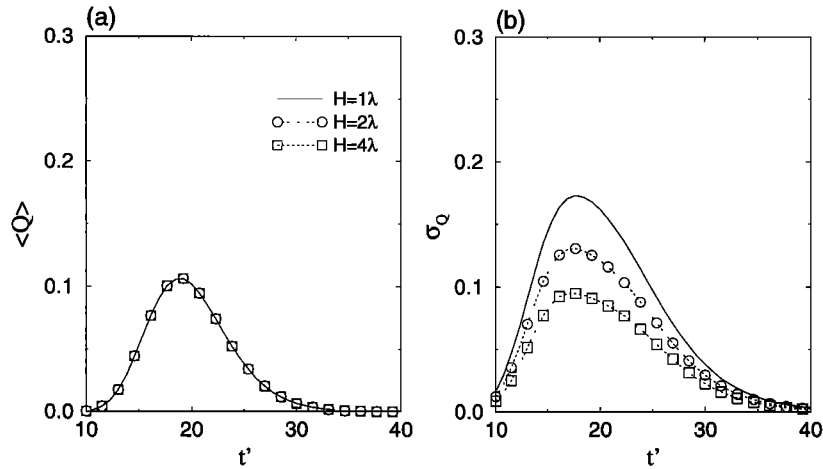
### 5.1. Stationary Flow Case

In this example, reactive and nonreactive solutes are introduced instantaneously into a uniform mean flow in unbounded, heterogeneous porous media. In this case the mean velocity  $\mathbf{U} = (U_1, 0)^T$  is constant. The velocity covariance functions are available analytically [Rubin, 1990]. With these velocity moments the statistical moments of travel time and transverse displacement can be computed, then the expected solute flux and the associated uncertainty can be evaluated. Cvetkovic *et al.* [1992] and Selroos and Cvetkovic [1994] have studied the first two moments of solute discharge (total solute flux)  $Q$  for nonreactive and reactive solutes in such a flow field, respectively. This is a special case of our approach for a nonstationary flow field. Figure 1 shows the moments of the total solute flux  $Q$  across a specific control plane (CP) as a function of dimensionless time  $t'$  for nonreactive and reactive solutes. The dimensionless time is defined as  $t' = tU_1/\lambda$ , where  $\lambda$  is the correlation scale of the underlying log hydraulic conductivity field. The CP is normal to the mean flow and located at  $x = 20\lambda$ . For both reactive and nonreactive solutes the source of unit mass is a line of size  $H = 1\lambda$  centered at  $(x, y) = (0, 0)$  and normal to the mean flow. The variance of the log hydraulic conductivity,  $\sigma_Y^2$ , is 0.5 as given by Cvetkovic *et al.* [1992], and the mean velocity  $U_1 = 1[T/L]$ . For the case of nonreactive solute the expected value  $\langle Q \rangle$  and the standard deviation  $\sigma_Q$  match the literature results [Andricevic and Cvetkovic, 1988,

Figure 1; Cvetkovic *et al.*, 1992, Figure 4]. For the reactive case, solute undergoes a sorption-desorption reaction controlled by first-order kinetics with  $k_0 = 0$ ,  $K_d = 1.0$ , and  $\alpha = 0.05$ . It is seen that for the reactive case,  $\langle Q \rangle$  has a lower peak and a longer tail than for the nonreactive case. This tailing effect due to mass transfer between the liquid and solid phases has been well studied for stationary flows [Cvetkovic and Dagan, 1994; Selroos and Cvetkovic, 1994; Andricevic and Cvetkovic, 1998]. Though not shown here, our results for CP at  $x = 10\lambda$  and  $\sigma_Y^2 = 1$  match those by Selroos and Cvetkovic [1994, Figures 2 and 3].

Figure 2 shows the total solute flux  $Q$  moments as a function of the source dimension in the absence of reaction. In all three cases shown, the solute of unit mass is distributed uniformly along a line of varying length  $H$ . The setup for these cases is the same as the nonreactive case shown in Figure 1. For the case of  $H = 1\lambda$ , as also seen in Figure 1, the standard deviation  $\sigma_Q(t')$  is generally larger than the expected value  $\langle Q \rangle(t')$ , reflecting a large uncertainty in predicting the total solute flux across the CP. This uncertainty is due to the incomplete knowledge of the spatial variability of the hydraulic conductivity field between the source and the CP. This uncertainty, however, decreases with the size of the source. The peak standard deviation of  $Q$  is smaller than its expected value  $\langle Q \rangle$  when  $H = 4\lambda$ , while  $\langle Q \rangle$  is not affected by the source dimension in this stationary flow field. When the source dimension is large enough,  $\sigma_Q$  becomes sufficiently small, and then the so-called ergodic limit is reached. This has recently been studied thoroughly by, for example, Dagan [1991], Cvetkovic *et al.* [1992], Zhang *et al.* [1996], and Andricevic and Cvetkovic [1998].

To compute the total solute flux  $Q$  moments, only the marginal travel time PDFs  $f_1(\tau)$  and  $f_2(\tau_1, \tau_2)$  are required (see Table 1). However, the joint one- and two-particle travel time and transverse displacement PDFs  $f_1(\tau, \eta)$  and  $f_2(\tau_1, \eta_1; \tau_2, \eta_2)$  are needed in order to compute the first two moments of (point) solute flux  $q$ . It has been recognized [e.g., Dagan *et al.*, 1992; Cvetkovic *et al.*, 1992; Cvetkovic and Dagan, 1994; Selroos and Cvetkovic, 1994] that  $\tau(x, \mathbf{a})$  and  $\eta(x, \mathbf{a})$  are uncorrelated in the stationary case of uniform mean flow such that  $f_1[\tau(x; \mathbf{a}), \eta(x; \mathbf{a})] = f_1[\tau(x; \mathbf{a})]f_1[\eta(x; \mathbf{a})]$ . In the literature this



**Figure 2.** (a) Expected value  $\langle Q \rangle$  and (b) standard deviation  $\sigma_Q$  of total solute flux across the control plane at  $x = 20\lambda$  as a function of dimensionless time for various source dimensions  $H$  (stationary flow case).

treatment has been generalized to the case of two particles by letting  $f_2[\tau_1(x; \mathbf{a}), \eta_1(x; \mathbf{a}); \tau_2(x; \mathbf{b}), \eta_2(x; \mathbf{b})] = f_2[\tau_1(x; \mathbf{a}), \tau_2(x; \mathbf{b})]f_2[\eta_1(x; \mathbf{a}), \eta_2(x; \mathbf{b})]$  [e.g., *Andricevic and Cvetkovic*, 1998]. (In the above,  $\mathbf{a} = (a_x, a_y)^T$  and  $\mathbf{b} = (b_x, b_y)^T$  are the starting positions of two particles.) For a spatially nonstationary flow this assumption is not valid because the joint moments  $\langle \tau'_1 \eta'_2 \rangle$  are generally nonzero.

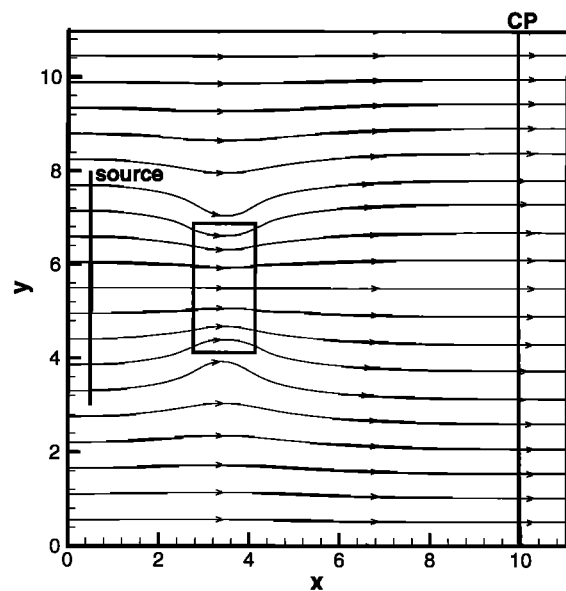
For a stationary velocity field, however, the validity of this assumption depends on the starting positions of the two particles (or the configuration of a solute source). In such a flow field the joint moment  $\langle \tau'_1(x; \mathbf{a}) \eta'_2(x; \mathbf{b}) \rangle$  can be rewritten from (39) as

$$\langle \tau'_1(x; \mathbf{a}) \eta'_2(x; \mathbf{b}) \rangle = -\frac{1}{U_1^3} \int_{a_x}^x \int_{b_y}^y C_{u_{12}}(x' - x'', a_y - b_y) dx' dx'', \quad (49)$$

where  $C_{u_{12}}(x' - x'', a_y - b_y) = \langle u_1(x', a_y) u_2(x'', b_y) \rangle$ . The property of this velocity covariance has been studied in detail for a uniform mean flow in unbounded domains, in two dimensions by *Rubin* [1990] and in three dimensions by *Zhang and Neuman* [1992], to first order. For such a uniform mean flow,  $C_{u_{12}}(r_1, r_2)$  is zero along the horizontal ( $r_2 = 0$ ) and vertical ( $r_1 = 0$ ) axes and is generally nonzero otherwise; the cross covariance is axis-symmetric. Hence it is easily seen that the joint moment  $\langle \tau' \eta' \rangle$  is zero, to first order, for either one particle or two particles starting from a line parallel to the mean flow (i.e.,  $r_2 = 0$ ). Another special case is that the two particles start from a line normal to the mean flow (i.e.,  $a_x = b_x$ ) such that the two integrals in (49) have the same limits. That the double integration is zero under this condition can be proven with the axis-symmetry property of the cross velocity covariance, namely,  $C_{u_{12}}(-r_1, r_2) = -C_{u_{12}}(r_1, r_2)$ . When the line formed by the starting positions of the two particles is neither parallel nor normal to the mean flow, the two-particle moment  $\langle \tau' \eta' \rangle$  is generally nonzero, even for stationary flows. Therefore, for a stationary flow, the correlation between two particles can be neglected when the solute source is a line either parallel or normal to the mean flow, but it needs to be included in the computation of  $\sigma_q$  for any other source configuration.

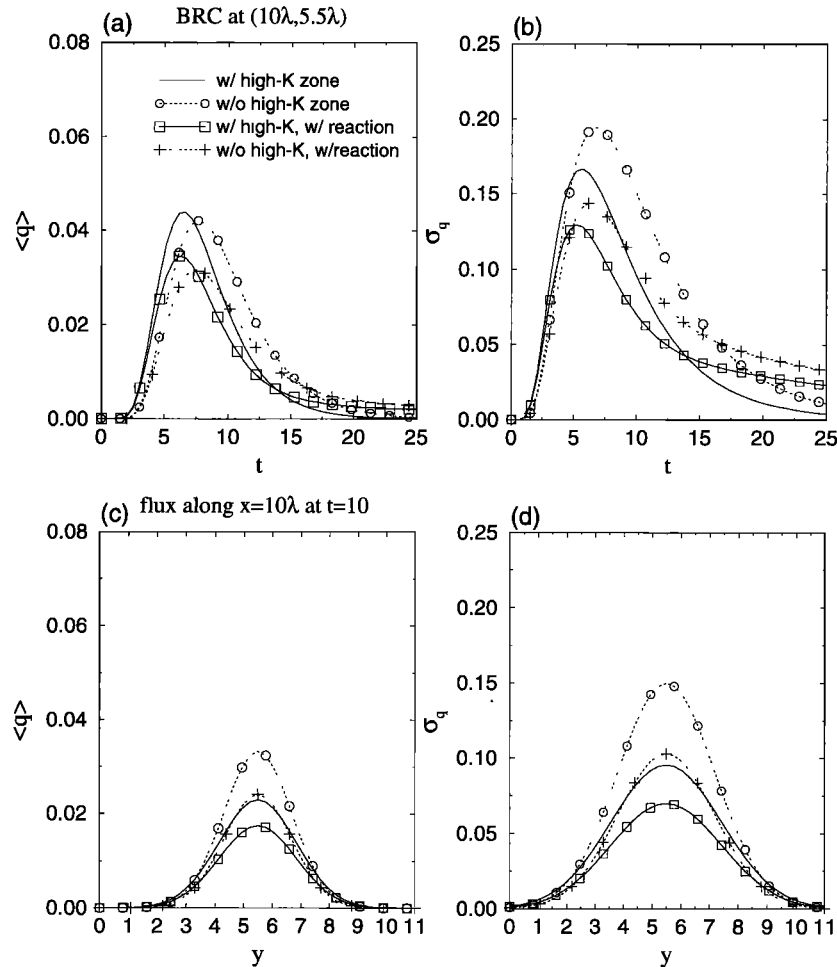
## 5.2. Nonstationary Flow Cases

In this subsection we show some examples of conservative and reactive solute transport in spatially nonstationary flow fields. The first example involves a high-permeability zone in an otherwise stationary permeability field. Figure 3 shows a sketch of the flow domain where the rectangle of size  $1.375\lambda$  by  $2.75\lambda$  centered at  $(3.4375\lambda, 5.5\lambda)$  is the high-permeability zone with  $\langle Y \rangle = 2$ , and it also depicts some streamlines of the mean flow field. The mean log hydraulic conductivity is  $\langle Y \rangle = 0$  (with geometric mean conductivity being  $1[L/T]$ ) for the rest of the domain. As mentioned earlier, the fluctuations of  $Y$  are assumed to be second-order stationary. We let  $\sigma_Y^2 = 1$  and  $\lambda = 1[L]$ . The boundary conditions are specified as follows: no-flow for the lower ( $y = 0$ ) and upper ( $y = 11\lambda$ ) boundaries, constant head ( $h = 11\lambda$ ) for the left ( $x = 0$ ) side, and



**Figure 3.** Sketch of a flow domain, the locations of source, control plane (CP), high-permeability zone, and the mean streamlines (high-permeability zone case).



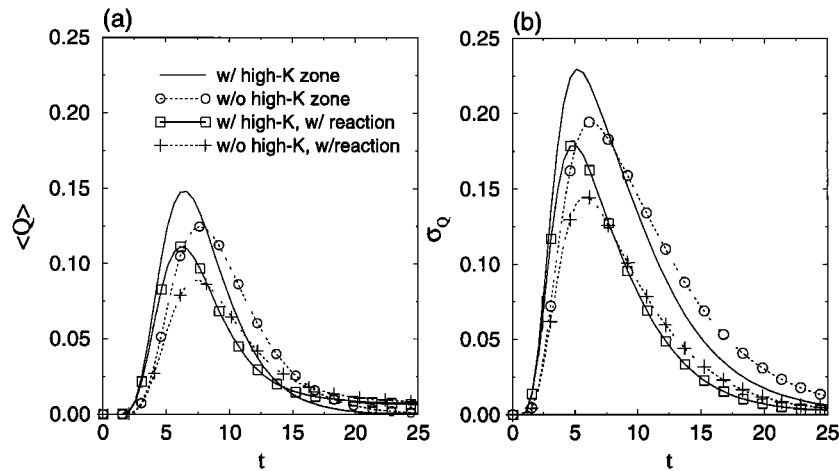


**Figure 4.** (a) Expected value  $\langle q \rangle$  and (b) standard deviation  $\sigma_q$  of point solute flux due to a source of length  $1\lambda$  across the control plane at  $x = 10\lambda$  (a and b) as a function of time and (c and d) as a function of transverse displacement with or without the high-permeability zone and with or without reaction.

constant head ( $h = 0$ ) for the right ( $x = 11\lambda$ ) side. Even under these simple boundary conditions the flow is nonstationary in that the velocity moments are location-dependent. Figure 4 shows the first two moments of  $q$  for four cases. For all four cases the line source of unit mass is of size  $H = 1\lambda$  centered at  $(0, 5.5\lambda)$ , and the CP is located at  $x = 10\lambda$ . The first two cases are for conservative solutes, and the last two cases are for reactive solutes. There is no high-permeability zone in the second case. In the third case both reaction and the high-permeability zone are present. The reactive parameters are the same as those for Figure 1. In Figures 4a and 4b we present the  $\langle q \rangle$  and  $\sigma_q$  profiles, respectively, for the plume center at the CP (i.e., at point  $(10\lambda, 5.5\lambda)$ ) as a function of time. From now on, we work with the absolute time  $t$  because a consistent dimensionless time may not be meaningfully defined with varying mean velocities in a nonstationary flow field. Comparing the two cases without reaction, the inclusion of a high-permeability zone renders an earlier solute arrival (i.e., faster advection), a higher peak for  $\langle q \rangle$  (i.e., less spreading), and a lower peak for  $\sigma_q$  (i.e., less uncertainty). It is apparent by comparing the two cases with reaction that the inclusion of a high-permeability zone has the same effect on reactive solutes. The inclusion of a low-permeability zone would have an opposite effect. Comparing the two cases with a high-permeabil-

ity zone, the sorption kinetics causes an increased tailing in the breakthrough with a decrease in the peak values of  $\langle q \rangle$  and  $\sigma_q$ . Figures 4c and 4d show the  $\langle q \rangle$  and  $\sigma_q$  profiles, respectively, as a function of transverse location on the CP for  $t = 10$ . It is seen that both  $\langle q \rangle$  and  $\sigma_q$  have Gaussian-type (single modal) profiles in the transverse direction for this and later times we checked. Figure 5 shows the profiles of the total solute flux  $Q$  moments across the control plane at  $x = 10\lambda$  as a function of time. The observations for the moments of the total solute flux  $Q$  are similar to those for the moments of the solute flux  $q$  at a particular point except that the peak standard deviation of  $Q$  is larger in the case of a high-permeability zone than in the case of stationary media. However, a comparison between Figures 4a and 4b and Figures 5a and 5b reveals that the relative uncertainty in predicting  $Q$  is much less than that with  $q$ . As expected, it should be much easier to predict solute flux across a plane than a point.

Figure 6 shows the  $\langle q \rangle$  and  $\sigma_q$  profiles for conservative solute of a larger source area in the same flow field. The solute of unit mass is uniformly distributed along a line of  $5\lambda$  centered at  $(0, 5.5\lambda)$  (see Figure 3), and the CP is also located at  $x = 10\lambda$ . In this case the source is wider than the high-permeability zone. At  $t = 15$  the profiles along the CP are single modal, as in the case of a smaller source dimension shown in Figures 4c



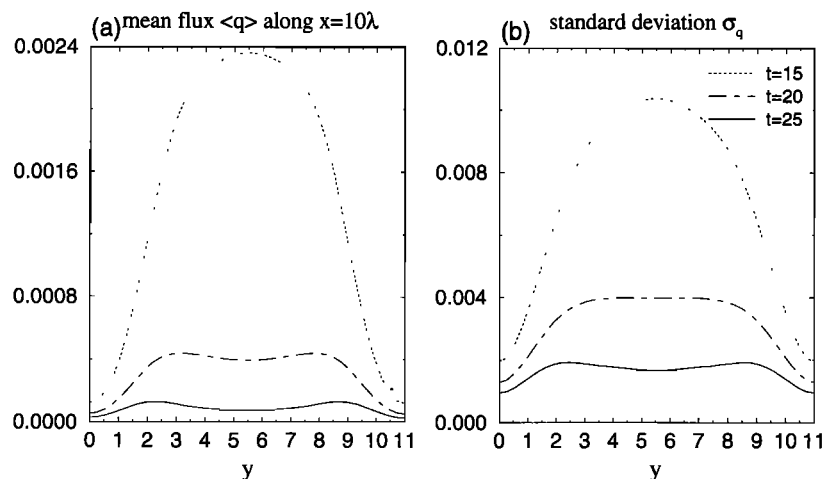
**Figure 5.** (a) Expected value  $\langle Q \rangle$  and (b) standard deviation  $\sigma_Q$  of total solute flux due to a source of length  $1\lambda$  across the control plane at  $x = 10\lambda$  as a function of time with or without the high-permeability zone and with or without reaction.

and 4d. At  $t = 20$  the mean profile is bimodal, while the standard deviation is still unimodal; at  $t = 25$  both profiles are bimodal. This indicates that the different parts of the plume travel at different velocities. Thus it is seen that the behavior of solute flux moments strongly depends on the configuration of nonstationary medium features and the source dimension and location. It is of interest to note that although it presumes the particle PDFs to be of single modal type (normal or lognormal), the nonstationary approach may yield non-Gaussian (multiple modal) behaviors for the solute flux moments in the presence of nonstationary flows. These non-Gaussian behaviors for a solute source of uniform concentration cannot be reproduced with a stationary approach in which the medium stationary features are ignored intentionally.

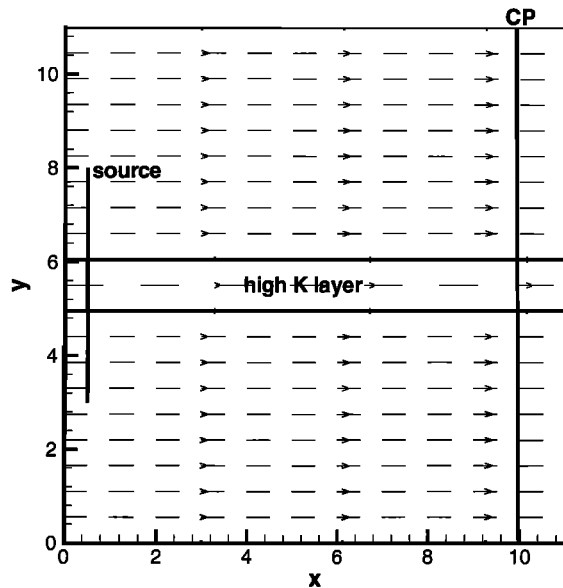
The next example studies solute transport in a field with a high-permeability layer (or channel). Figure 7 shows a sketch of the setup. The layer of width  $1.1\lambda$  in the domain center has a higher mean log hydraulic conductivity  $\langle Y \rangle$  ( $= 0.2$  or  $0.5$ ) than does the rest of the domain ( $\langle Y \rangle = 0$ ). As expected, this high-permeability layer yields a fast flow path. We investigate

the impact of this fast flow path on uncertainty estimates of solute flux. Figure 8 shows the total solute flux  $Q$  moments due to a source of unit mass distributed over a line of size  $H = 1\lambda$  as a function of time. Like in the previous example, we let  $\sigma_Y^2 = 1$  and  $\lambda = 1[L]$ . Compared to the case of constant  $\langle Y \rangle$ , the high-permeability layer in the domain center renders an earlier arrival (indicating faster advection) and more compact profiles with higher peak values (indicating less temporal spreading) for both the mean and standard deviation of the breakthrough curves. It is seen that the standard deviation of  $Q$  is generally larger than the expected value, indicating a significant level of uncertainty caused by the incomplete knowledge of the spatial variability of the underlying permeability field. As discussed earlier, this uncertainty decreases with the increase of the source dimension.

The last example looks at solute transport in a trending permeability field. This trending in permeability may be caused by, for example, downward or upward sand coarsening or periodic sand/shale patterns. The domain is of size  $11\lambda$  by  $11\lambda$  with the same boundary conditions as for the case shown in



**Figure 6.** (a) Expected value  $\langle q \rangle$  and (b) standard deviation  $\sigma_q$  of point solute flux due to a source of length  $5\lambda$  across the control plane at  $x = 10\lambda$  as a function of transverse displacement at  $t = 15, 20$ , and  $25$  (high-permeability zone case).



**Figure 7.** Sketch of a flow domain, the locations of source, control plane (CP), high-permeability zone, and the mean streamlines (high-permeability layer case).

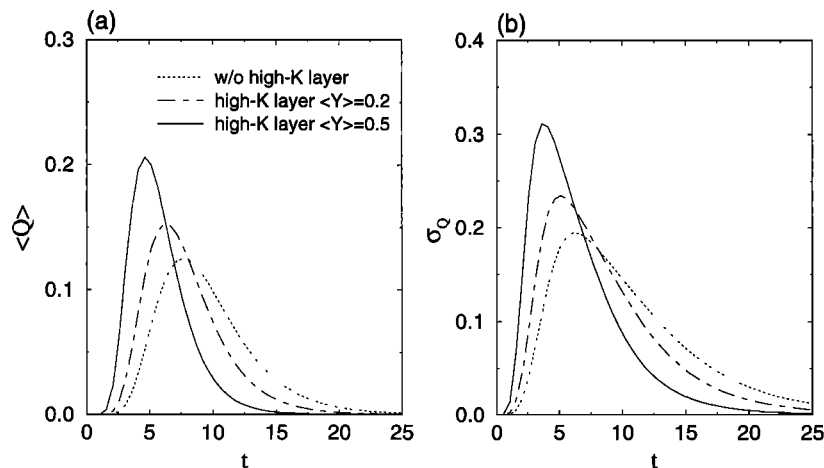
Figure 3. The mean log hydraulic conductivity varies linearly from left to right:  $\langle Y(x) \rangle = Y_0 - 0.05x$  with  $Y_0 = 0$  being the mean value at  $x = 0$ . Note that under these conditions, the (zeroth or first order) mean velocity is unidirectional and uniform spatially [Zhang, 1998]. However, the velocity covariance is nonstationary (location dependent) because of the combined effects of trending in  $Y$  and the boundaries. Figure 9 shows the total solute flux  $\langle Q \rangle$  and  $\sigma_Q$  profiles as a function of time. Compared to the case of constant  $\langle Y \rangle$ , the linear trend in  $Y$  renders a later arrival (indicating slower advection) and fatter profiles with lower peak values (indicating more temporal spreading). A trend with increasing permeability would yield an opposite effect. The finding for the case of linearly trending permeability parallel to the mean flow is consistent with that of Indelman and Rubin [1996], already mentioned in the introduction. These authors evaluated particle displacement covariances and macrodispersion coefficients for various linear trends

in permeability and found that the longitudinal dispersion coefficient is smaller in the case of increasing linear trend parallel to the mean flow than in the case of stationary media.

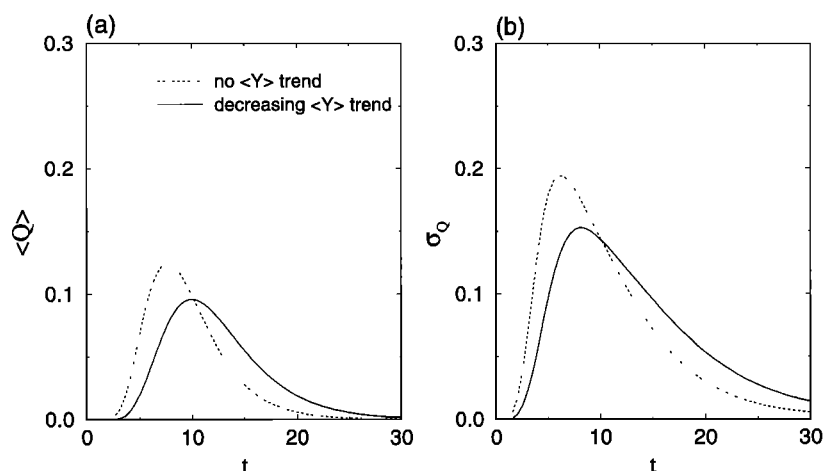
## 6. Summary and Discussion

A theoretical framework for solute flux through spatially nonstationary flows in porous media is developed. The flow nonstationarity may stem from medium nonstationarity (or multiscale structure and heterogeneity), finite domain boundaries, and/or fluid pumping and injecting. The problem of solute flux is formulated from a Lagrangian viewpoint in such a flow field. The solute flux statistics (mean and variance) are expressed in terms of the probability density functions (PDFs) of the particle travel time and transverse displacement. It has been found reasonable in the literature to approximate the travel time with a lognormal distribution and to approximate transverse displacement with a (truncated) normal distribution. With this Lagrangian closure the evaluation of the particle PDFs becomes that of the first two moments of travel time and displacement. In stationary flows the latter moments are simple functions of the velocity moments. However, for nonstationary flows they are much more complex. We derived general expressions for the travel time and transverse displacement moments in terms of the nonstationary velocity moments.

We illustrated the general approach with some examples of conservative and reactive solute transport in stationary and nonstationary flows. The purpose of the examples involving stationary flow is to compare with published results. It is found that we were able to reproduce the literature results for stationary flows with the more general nonstationary approach. We also investigated the validity of the common assumption made earlier that the travel time and transverse displacement are uncorrelated. We confirmed that for stationary flows the travel time and transverse displacement are uncorrelated for a single particle. However, these two quantities are correlated for two different particles even with stationary flows except for some special solute configurations, contrary to the common assumption. As an exception, these two quantities are uncorrelated for a line source when it is either parallel or normal to the mean flow. For nonstationary flows the travel time and transverse displacement are generally correlated. Although it



**Figure 8.** (a) Expected value  $\langle Q \rangle$  and (b) standard deviation  $\sigma_Q$  of total solute flux due to a source of length  $1\lambda$  across the control plane at  $x = 10\lambda$  as a function of time with a layer of different mean log hydraulic conductivity  $\langle Y \rangle$  (high-permeability layer case).



**Figure 9.** (a) Expected value  $\langle Q \rangle$  and (b) standard deviation  $\sigma_Q$  of total solute flux due to a source of length  $1\lambda$  across the control plane at  $x = 10\lambda$  as a function of time with and without a linear trend in the mean permeability.

makes the math more complicated, it is important to account for this correlation. The other examples investigate the effects of flow nonstationarity on the prediction of reactive and non-reactive solute flux and the associated uncertainty. In our examples the flow nonstationarity is due to the combined effects of medium nonstationarity (or multiscale structure and heterogeneity) and finite boundaries. It is found that based on these examples the flow nonstationarity has a strong impact on predicting solute flux across a control plane and on the corresponding prediction uncertainty. For example, the inclusion of a high-permeability zone or channel between the solute source and the control plane renders faster advection and less spreading; a decreasing linear trend in the mean hydraulic conductivity yields slower advection and larger temporal spreading. In a word, the behavior of solute flux moments strongly depends on the configuration of medium nonstationary features and the source dimension and location. The developed nonstationary approach may result in non-Gaussian (multiple modal) yet realistic behaviors for solute flux moments in the presence of flow nonstationarities, while these non-Gaussian behaviors may not be reproduced with a traditional stationary approach.

The examples shown in this paper involve some relatively simple configurations of medium nonstationary features. These examples are selected to illustrate the approach. The general approach is, however, applicable to more complex patterns of flow nonstationarities caused either by medium nonstationary features (such as distinct macroscale inclusions, layerings, and geologic structures) or by realistic flow configurations (such as fluid pumping and injecting). A more complex configuration of medium nonstationarity may be a combination of a number of such features shown in this paper. Below we outline the general procedure for applying this approach to more complex situations. With identified medium nonstationary features and flow configurations the semianalytical flow approach of Zhang [1998] and Zhang and Winter [1999] can be used to compute the nonstationary velocity moments. Then the first two moments of travel time and transverse displacement are evaluated numerically with the general expressions developed in the present study. Finally, the travel time and transverse displacement PDFs are constructed with the latter moments, and the first two moments of solute flux across a control plane can be evaluated with these PDFs. The

first moment (mean) is an estimate of the solute flux, and the second moment (standard deviation) is a measure of uncertainty associated with the estimation. These two moments can be used to construct confidence intervals for solute flux at each point on the control plane or the total solute flux across it. Furthermore, these moments serve as an input for risk assessment of contaminants migrating in complex, heterogeneous porous media.

The theoretical framework presented in the paper involves two major assumptions: first-order approximations and neglect of local (pore scale) dispersion. First, the first-order (small variance) approximations are invoked in deriving the general expressions of the travel time and transverse displacement moments as well as in obtaining the flow moments. Theoretically, it requires the variance of log hydraulic conductivity to be much smaller than unity. However, many studies involving stationary flows [e.g., Chin, 1997; Zhang and Winter, 1999] revealed that the first-order stochastic flow and transport theories are quite robust and applicable to a moderate variance. Furthermore, as pointed out by Zhang [1998], accounting for nonstationary features in a hydraulic conductivity field reduces the underlying variance. Hence the small-variance assumption may be even more justified for the approaches that take medium nonstationarities into consideration. Second, local dispersion is neglected in the Lagrangian approach utilized to derive the general framework of solute flux. This is a shortcoming of the general approach. Although local dispersion may not significantly affect the expected values of solute flux, it may impact the estimation of the prediction uncertainty to a larger extent especially at late times [e.g., Kapoor and Gelhar, 1994]. Since the inclusion of local dispersion may reduce the uncertainty associated with the prediction of solute flux, the prediction uncertainty presented in this paper may constitute an upper bound. However, as one should expect, the effect of local dispersion decreases with the decrease of local dispersivity. A recent study by Zhang and Neuman [1996] concluded that when local dispersion is small relative to macrodispersion, its effect on the prediction of resident concentration at finite times can, for all practical purposes, be disregarded. Hence we expect that the developed framework with neglect of local dispersion provides a good estimation of solute flux and the prediction uncertainty in nonstationary flow fields when local

dispersion is small. When local dispersion is significant, so may be its effect on the prediction uncertainty. In the latter case this approach provides an upper bound (and conservative) estimation of the prediction uncertainty.

## Appendix

With (32) we may rewrite (33) as

$$\frac{d\eta'(x; \mathbf{a})}{dx} U_1(x, \langle \eta \rangle) = u_2(x, \langle \eta \rangle) - \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle) + \eta' \left[ \frac{\partial U_2(x, \eta)}{\partial \eta} - \frac{d\eta}{dx} \frac{\partial U_1(x, \eta)}{\partial \eta} \right]_{\eta=\langle \eta \rangle}. \quad (\text{A1})$$

In the absence of a sink/source, for steady state flow we have  $\nabla \cdot \mathbf{V} = 0$ . With  $V_i = U_i + u_i$ , this can be rewritten in two-dimensions as

$$\frac{\partial U_1(x, y)}{\partial x} + \frac{\partial U_2(x, y)}{\partial y} + \frac{\partial u_1(x, y)}{\partial x} + \frac{\partial u_2(x, y)}{\partial y} = 0. \quad (\text{A2})$$

Taking ensemble mean of (A2) yields

$$\frac{\partial U_1(x, y)}{\partial x} + \frac{\partial U_2(x, y)}{\partial y} = 0. \quad (\text{A3})$$

This equation is true for every point in regions free of sink/source. Hence at  $y = \langle \eta(x) \rangle$  we have

$$\left[ \frac{\partial U_1(x, \eta)}{\partial x} + \frac{\partial U_2(x, y)}{\partial y} \right]_{y=\langle \eta \rangle} = 0. \quad (\text{A4})$$

Hence (A1) can be further simplified into

$$\begin{aligned} \frac{d\eta'(x, \mathbf{a})}{dx} U_1(x, \langle \eta \rangle) &= u_2(x, \langle \eta \rangle) - \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle) \\ &- \eta' \left[ \frac{\partial U_1(x, \eta)}{\partial x} + \frac{d\eta}{dx} \frac{\partial U_1(x, \eta)}{\partial \eta} \right]_{\eta=\langle \eta \rangle} = u_2(x, \langle \eta \rangle) \\ &- \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle) - \eta' \frac{dU_1(x, \langle \eta \rangle)}{dx}. \end{aligned} \quad (\text{A5})$$

In (A5) we have used that  $dU_1(x, \eta)/dx = \partial U_1(x, \eta)/\partial x + [d\eta/dx] \partial U_1(x, \eta)/\partial \eta$ . Since  $d[\eta' U_1(x, \langle \eta \rangle)]/dx = U_1(x, \langle \eta \rangle) d\eta'/dx + \eta' dU_1/dx$ , we have

$$\begin{aligned} \frac{d[\eta'(x; \mathbf{a}) U_1(x, \langle \eta \rangle)]}{dx} &= u_2(x, \langle \eta \rangle) \\ &- \frac{U_2(x, \langle \eta \rangle)}{U_1(x, \langle \eta \rangle)} u_1(x, \langle \eta \rangle), \end{aligned} \quad (\text{A6})$$

which can be rewritten as (34).

**Acknowledgments.** This work was partially funded by LDRD/ER project 99025 from Los Alamos National Laboratory, which is operated by the University of California for the U.S. Department of Energy. The authors wish to thank Thomas Harter, two anonymous reviewers, and the Associate Editor for their helpful comments on this paper.

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(Received September 17, 1999; revised March 27, 2000; accepted March 28, 2000.)