

Relative dispersion for solute flux in aquifers

By ROKO ANDRIČEVIĆ AND VLADIMIR CVETKOVIĆ

¹ Desert Research Institute, Water Resources Center, University System of Nevada, Las Vegas, NV 89132, USA

² Division of Water Resources Engineering, Royal Institute of Technology, Stockholm, Sweden

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The relative dispersion framework for the non-reactive and reactive solute flux in aquifers is presented in terms of the first two statistical moments. The solute flux is described as a space–time process where time refers to the solute flux breakthrough and space refers to the transverse displacement distribution at the control plane. The statistics of the solute flux breakthrough and transversal displacement distributions are derived by analysing the motion of particle pairs. The results indicate that the relative dispersion formulation approaches the absolute dispersion results on increasing the source size (e.g. > 10 heterogeneity scales). The solute flux statistics, when sampling volume is accounted for, show a flattened distribution for the solute flux variance in the space–time domain. For reactive solutes, the solute flux shows a tailing phenomenon in time while solute flux variance exhibits bi-modality in transverse distribution during the recession stage of the solute breakthrough. The solute flux correlation structure is defined as an integral measure over space and time, providing a potentially useful tool for sampling design in the subsurface.

1. Introduction

The quality of subsurface waters and strong reliance on its purity for groundwater supply are important current environmental issues. Hazardous waste storage and particularly the high-level radioactive waste sites pose a long-term threat to the integrity of subsurface environments. Potential toxicity of contaminated groundwater and associated health risks depend directly on contaminant concentrations. Thus our ability to accurately predict concentration magnitude is critical in risk assessments and remedial decisions. Although the same can be said for surface waters and the atmosphere, the peculiarities of geological environments require specific approaches suitable for studying the contaminant plume dispersion in groundwater flows.

Unlike the surface water and atmosphere, where most flows are turbulent, the subsurface flows are for most cases slow (laminar) and steady flows of an incompressible fluid. The simplified Navier–Stokes equations when applied to such subsurface flows result in a macroscopic law that can be compared with Darcy’s experimental law (Matheron 1967). However, the tortuous and unpredictable pathways of groundwater flows resulting from natural geological heterogeneity yield contaminant concentrations that are random fields, i.e. describable only in a statistical sense. Although this is similar to random concentrations in surface water, or the atmosphere, the heterogeneity of the flow is clearly of different origin.

The spreading of contaminants in environmental flows is a major conceptual and practical challenge. The predictive models are concerned with evaluating the statistical properties of concentration fields. In atmospheric turbulence the concept of relative

dispersion was introduced by Richardson (1926) and further elaborated by Batchelor (1952), Sullivan (1971), and Chatwin & Sullivan (1979). The key features were that scales of turbulence larger than the cloud size would simply advect the cloud; scales much smaller would result in a diffusion mechanism, and scales comparable to the cloud size would distort the cloud in an irregular manner. Complementary to this theoretical work on relative dispersion, numerical simulation models were developed and used for predicting the spreading of a single cloud. So called two-tracer models developed by Thompson (1990), Borgas & Sawford (1994), and Faller (1996) are based on tracing the motion of particle pairs in turbulent flows. These models follow a Monte-Carlo approach and they are commonly based on Eulerian velocity correlations, except the work by Faller (1996) who employed the two-tracer second-order Lagrangian relations.

Most efforts in studying subsurface contaminant transport have focused on quantifying the expected concentration where the ensemble is a set of realizations of subsurface aquifers resulting from the geological heterogeneity (e.g. Gelhar & Axness 1983; Dagan 1984; Rubin 1990; Neuman 1993; Graham & McLaughlin 1989; Cushman & Ginn 1993). This approach yields absolute dispersion which contains random advection of the plume as a whole. More recently, studies have focused on 'non-ergodic' transport, i.e. on transport where the plume size is small or comparable to the scale of heterogeneity such that plume meandering may be significant. In particular, the second spatial moment for non-reactive solute has been evaluated by removing the effect of plume meandering (relative dispersion) (e.g. Kitanidis 1988; Dagan 1991; Rajaram & Gelhar 1993; Zhang, Zhang & Ling 1996). Using the derived second spatial moment for relative dispersion, expected relative concentration can be quantified, for instance, by assuming a Gaussian distribution; this distribution is likely to be more consistent with an average spatial concentration distribution that would be observed in a single realization.

A useful representation of transport in aquifers is by the 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 (e.g. Kreft & Zuber 1978; Dagan, Cvetkovic & Shapiro 1992). The flux-averaged concentration is consistent with common procedures for measuring concentrations in laboratory columns, in soils, as well as in aquifers (e.g. Kreft & Zuber 1978; Shapiro & Cvetkovic 1988). The solute discharge defined as the flux integrated over a control surface was considered as a prime quantity of interest in a number of studies (e.g. Cvetkovic & Shapiro 1990; Dagan & Nguyen 1989; Cvetkovic, Dagan & Shapiro 1992; Destouni & Graham 1995; Andričević & Cvetković 1996; Selroos 1997*a, b*). Current regulatory standards for the subsurface environment, especially those set in terms of travel time, make the solute flux approach an appealing framework for predicting subsurface contaminant transport. To describe the absolute dispersion of solute discharge, the probability density function (p.d.f.) of particle travel time from a fixed origin is required. The second temporal moment for reactive and non-reactive solute where the effect of plume meandering is removed (relative dispersion) was investigated by Selroos (1995). Similarly to the results for concentration, the second temporal moment can be used to parameterize a travel time distribution which quantifies the relative solute discharge.

For most applications, the mean description of transport (in the form of concentration or mass flux) is insufficient. The requirement is a statistical description of the concentration, or the mass flux, as a function of space and time such that both trends and fluctuations are quantified. For all practical purposes this implies quantifying

the first two moments (mean and variance) and assuming a distribution that can be used say in risk and safety assessment (Andričević & Cvetković 1996). Groundwater velocity variations on a scale larger than the plume size ('plume meandering') generally influence the entire statistics of solute concentration, or mass flux. It is therefore important to evaluate in a relative sense not only the mean concentration or mass flux, but also the variance.

In this paper a theoretical framework for relative dispersion is proposed in terms of the solute mass flux, defined as mass per unit time and unit area through a control plane. The solute flux depends on the distribution of the transverse displacements and on solute travel time evaluated at a fixed control plane. The mean solute flux and solute flux standard deviation will be derived using the Lagrangian framework in a relative sense, i.e. the origin of coordinates will be at the centre of mass of the solute plume throughout each realization of the geologic media. The kinematics of a particle pair and two particle pairs will be used to evaluate the statistics required for describing the first two moments of the solute flux. The issue of common sampling practice in the subsurface and degree of averaging introduced during collection of measurements is directly incorporated in the solution and its effect analysed.

In §3, the Lagrangian transport formulation is outlined and solute mass flux defined. Section 4 formulates the solute flux statistics and correlation structure using the relative dispersion formulation. In §5 the case of uniform source distribution is presented. First-order results for the one and two particle-pair statistical moments are given in §6. Section 7 is devoted to the presentation of illustrative examples for both reactive and non-reactive solute transport.

2. Problem description

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, $\nabla \cdot (n\mathbf{V}) = 0$, and is related to the hydraulic conductivity and to the hydraulic head Φ through Darcy's law $\mathbf{V} = -(K/n)\nabla\Phi$, where n is the effective porosity. Furthermore, we assume that a mean (macroscopic, or field-scale) drift can be identified for the groundwater flow.

The heterogeneous flow implies irregular streamlines which in an average sense are parallel to the mean groundwater flow direction (figure 1a). We consider in this study a time-independent and statistically stationary $\mathbf{V}(V_x, V_y, V_z)$. Without loss of generality, the mean flow is taken in the direction x , i.e. $\mathbf{U}(U, 0, 0)$ where $\mathbf{U} \equiv \langle \mathbf{V} \rangle$ and angular brackets denote ensemble averaging. The mean and covariance function of \mathbf{V} are considered known, having been derived from the continuity equation and Darcy's law using the first-order approximation (e.g. Rubin & Dagan 1992).

At time $t = 0$, a solute of total mass M is released into the flow field 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 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, oriented normal to the flow and located at some distance from the source, through which the solute mass flux is to be predicted or measured; it is

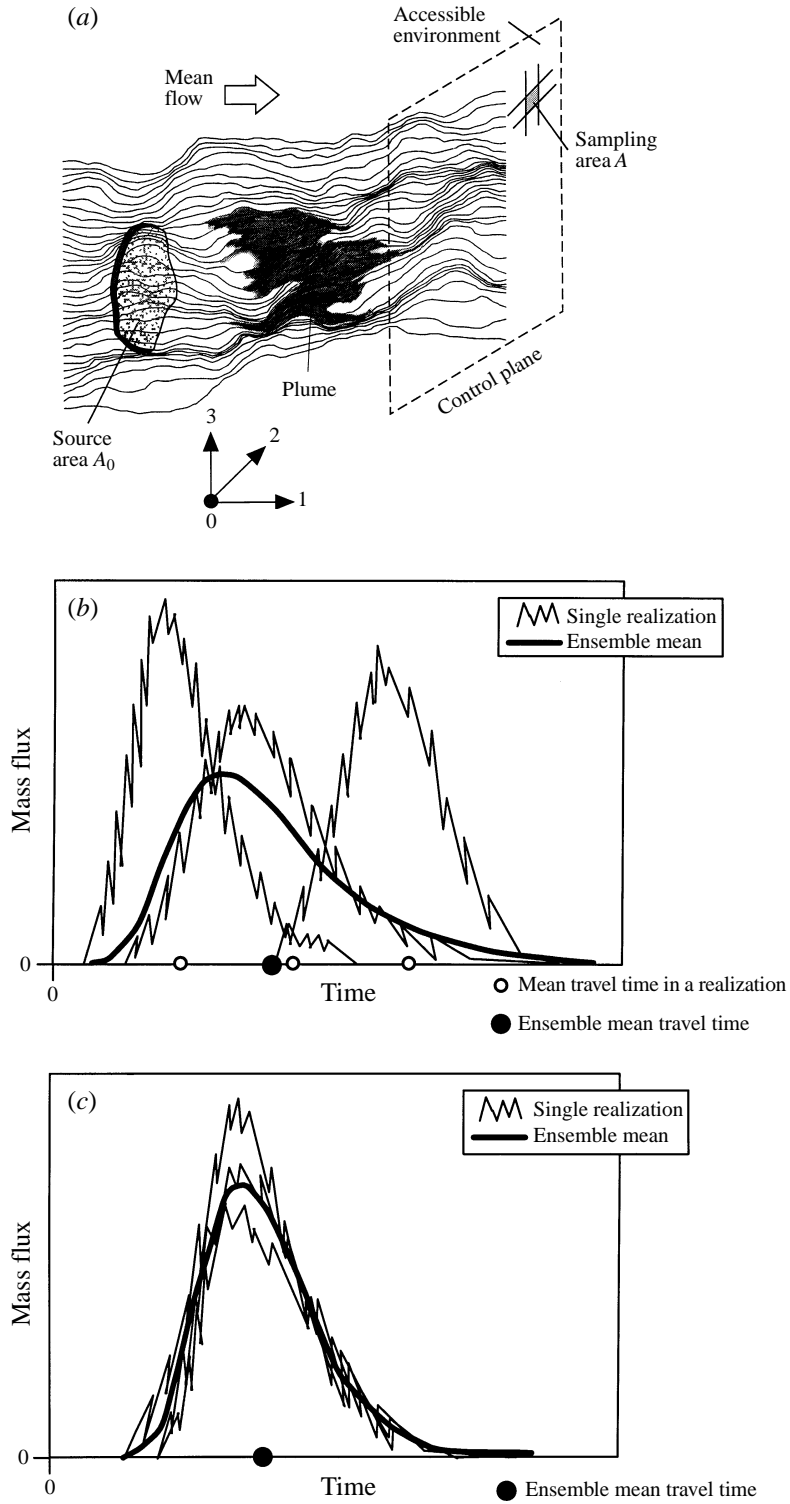


FIGURE 1. Problem configuration and solute flux breakthrough ensemble averaging: (a) problem configuration, (b) absolute dispersion and (c) relative dispersion.

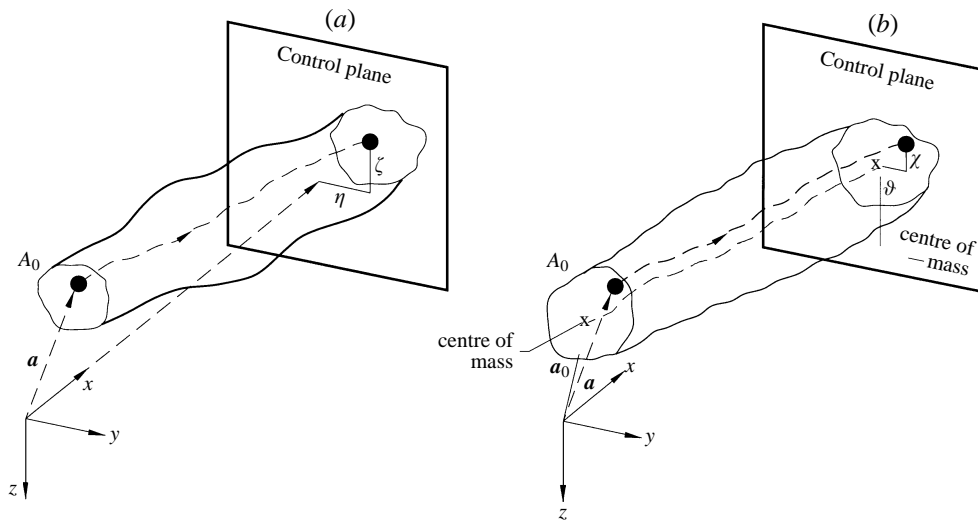


FIGURE 2. Definition sketch of particle displacement in (a) fixed frame of reference and (b) relative coordinates, for $\rho_0 = \text{const.}$

referred to as the *control plane* (CP) (figures 1a and 2). Owing to velocity fluctuations on a scale equal to and smaller than the plume size, the plume is diffused and distorted in an irregular manner (figure 1a). Velocity fluctuation on a scale larger than the plume size cause the plume to ‘meander’ relative to the mean flow direction.

For a qualitative description of transport, consider first the breakthrough of the solute plume across the entire control plane [MT^{-1}]. Figures 1(b) and 1(c) schematically show the difference between absolute and relative dispersion. The ensemble average for absolute dispersion accounts for both meandering and sub-plume velocity fluctuations; hence the dispersion is largest (figure 1b). Owing to relatively strong geological heterogeneity, the temporal distribution of mass arrival (breakthrough) may differ significantly from realization to realization yielding the ensemble average from the fixed origin being quite different from any realization of the solute breakthrough (figure 1b). By comparison, the effect of meandering is removed from ensemble averages for relative dispersion, such that the spreading is generally smaller, and more consistent with the breakthrough in individual realizations (figure 1c). The expected breakthrough for relative dispersion is obtained from plume realizations where the mean arrival times are set to coincide (figure 1c).

Next, consider the transverse position of the plume as it crosses the control plane. Figure 2 shows displacement trajectories of particles advected from the source, described in absolute coordinates (figure 2a) and coordinates relative to the mean transverse displacement (figure 2b).

The main objective of the present study is to derive the statistical moments (mean and variance) of the solute flux in relative coordinates. In contrast to the absolute dispersion which concentrates on a single particle, relative dispersion relates to particle pairs. Thus, we require the first two moments of travel time and transverse displacement probability density functions (p.d.f.s) based on the statistics of motion of particle pairs. In order to evaluate the solute flux variance, the joint p.d.f. between two particle pairs will be used. A particular problem to be addressed in the present study is how to define and compute a global measure of plume statistical structure in space and time, in analogy to the distance–neighbour function of Richardson (1926).

3. Lagrangian transport formulation

3.1. Kinematical relationships

Traditional description of advective transport is by the trajectory $\mathbf{X} = \mathbf{X}(t; \mathbf{a})$ where $\mathbf{X}(0; \mathbf{a}) = \mathbf{a}$ is the point of injection at $t = 0$ (Taylor 1921). The statistics of $\mathbf{X}(X_x, X_y, X_z)$ can be approximately related to the statistics of the groundwater velocity field, $\mathbf{V}(\mathbf{x})$, as well as to the statistics of the hydraulic conductivity (e.g. Dagan 1984).

In our following analysis we quantify advective transport by the Lagrangian space–time process $(\tau, \boldsymbol{\eta})$, rather than the space process \mathbf{X} (e.g. Dagan *et al.* 1992; Cvetković & Dagan 1994). $\tau(x; \mathbf{a})$ is a time process and quantifies the travel (arrival) time of the advective particle from the origin, $\mathbf{a}(0, a_y, a_z)$, to a control plane (CP) at x . We assume the solute parcel moves in the direction of the mean flow and τ is positive and finite. $\boldsymbol{\eta}(\eta, \zeta)$ is a space process that quantifies the transverse displacement, where $\boldsymbol{\eta}(0; \mathbf{a}) = \mathbf{a}$ (figure 2).

The travel time τ can be obtained formally as $\tau(x; \mathbf{a}) = X_x^{-1}(x; \mathbf{a})$, or explicitly as

$$\tau(x; \mathbf{a}) = \int_0^x \frac{d\xi}{V_x(\xi, \eta, \zeta)}. \quad (1)$$

The components of the transverse vector can be evaluated from X_y and X_z as

$$\eta(x; \mathbf{a}) = X_y[\tau(x; \mathbf{a}); \mathbf{a}], \quad \zeta(x; \mathbf{a}) = X_z[\tau(x; \mathbf{a}); \mathbf{a}], \quad (2)$$

or from the velocity field explicitly as

$$\eta(x; \mathbf{a}) = \int_0^x \frac{V_y(\xi, \eta, \zeta)}{V_x(\xi, \eta, \zeta)} d\xi, \quad \zeta(x; \mathbf{a}) = \int_0^x \frac{V_z(\xi, \eta, \zeta)}{V_x(\xi, \eta, \zeta)} d\xi. \quad (3)$$

Equations (1)–(3) provide the basic random variables for a single advecting solute particle.

The basic random variables that quantify the advection of the plume as a whole are the areally averaged travel time and transverse displacement defined as

$$T(x; A_0) \equiv \frac{1}{A_0} \int_{A_0} \tau(x; \mathbf{a}) d\mathbf{a}, \quad (4)$$

$$\mathbf{Y}(x; A_0) \equiv \frac{1}{A_0} \int_{A_0} \boldsymbol{\eta}(x; \mathbf{a}) d\mathbf{a}, \quad (5)$$

$T(x; A_0)$ and $\mathbf{Y}(x; A_0)$ [$Y(x; A_0), Z(x; A_0)$] represent the mean travel time and mean transverse displacement for the entire plume crossing the CP. We emphasize the dependence of T and \mathbf{Y} on the source size *and* the source shape, for notational simplicity denoted by A_0 . Both T (4) and \mathbf{Y} (5) are defined as kinematical quantities; only in the case of $\rho_0(a) = \text{const.}$, do T and \mathbf{Y} also represent the travel time and transverse displacement of the centre of mass of the plume.

The basic random variables for describing the state of *relative dispersion* of a plume of particles advected by a random velocity field, $\mathbf{V}(\mathbf{x})$, are

$$\left. \begin{aligned} \theta(x; \mathbf{a}, A_0) &\equiv \tau(x; \mathbf{a}) - T(x; A_0) = \frac{1}{A_0} \int_{A_0} \Delta\tau(x; \mathbf{a}, \mathbf{a}') d\mathbf{a}', \\ \boldsymbol{\vartheta}(x; \mathbf{a}, A_0) &\equiv \boldsymbol{\eta}(x; \mathbf{a}) - \mathbf{Y}(x; A_0) = \frac{1}{A_0} \int_{A_0} \Delta\boldsymbol{\eta}(x; \mathbf{a}, \mathbf{a}') d\mathbf{a}', \end{aligned} \right\} \quad (6)$$

with $\boldsymbol{\vartheta}(\vartheta, \chi)$; θ and $\boldsymbol{\vartheta}$ quantify fluctuations of the particle transport variables τ and $\boldsymbol{\eta}$

from the plume transport variables T and Y . In (6),

$$\Delta\tau(x; \mathbf{a}, \mathbf{a}') \equiv \tau(x; \mathbf{a}) - \tau(x; \mathbf{a}'), \quad \Delta\boldsymbol{\eta}(x; \mathbf{a}, \mathbf{a}') \equiv \boldsymbol{\eta}(x; \mathbf{a}) - \boldsymbol{\eta}(x; \mathbf{a}') \quad (7)$$

represent a travel time difference and transverse separation at the CP for a particle pair.

3.2. Solute mass flux and discharge

General mass balance equations for solute undergoing mass transfer reactions are

$$\frac{\partial C}{\partial t} + \mathbf{V} \cdot \nabla C = \psi_m(C, N), \quad \frac{\partial N}{\partial t} = \psi_{im}(C, N), \quad (8)$$

where we consider advection only, and where the fluid mass balance equation has been used. In (8), C is the mobile and N the immobile solute concentration, with the corresponding sink/source terms denoted as ψ_m and ψ_{im} . In the following we restrict our discussion to linear mass transfer reactions. Cvetkovic & 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. Note that for nonlinear reactions the retention function would depend on the initial and/or boundary concentration (e.g. Dagan & Cvetkovic 1996; Cvetkovic & Dagan 1996).

In aquifers, the migrating solute is detected from a single or an array of drilled wells (boreholes). The corresponding sampling area is denoted by A and its value will depend on the sampling method used. Thus we seek to predict the statistical properties of the solute flux averaged over A . Integrating the solute flux for a single particle, $\Delta q \equiv \rho_0(\mathbf{a}) d\mathbf{a} \Gamma(t, \tau) \delta(\mathbf{y} - \boldsymbol{\eta})$, over the injection area A_0 , averaging over the sampling area $A(\mathbf{y})$ centred at $\mathbf{y}(y, z)$ within the CP, yields the solute mass flux component orthogonal to the CP at x as

$$q(t, \mathbf{y}; x, A) = \frac{1}{A} \int_{A_0} \int_A \rho_0(\mathbf{a}) \Gamma(t, \tau) \delta(\mathbf{y}' - \boldsymbol{\eta}) d\mathbf{y}' d\mathbf{a}, \quad (9)$$

where

$$\Gamma(t, \tau) \equiv \int_0^t \phi(t - t') \gamma(t', \tau) dt' \quad (10)$$

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 (8), transformed onto an advection flow path (Cvetkovic & Dagan 1994). For instantaneous release, $\phi \equiv \delta(t)$; for non-reactive solute $\gamma \equiv \delta(t - \tau)$. For instantaneous release of non-reactive solute (10) yields $\Gamma = \delta(t - \tau)$. Note that the concentration C obtained from (8) and the solute flux for a single particle, Δq , are related as $\Delta q = C V_x(x, \boldsymbol{\eta}, \zeta)$.

The dependence of q on A emphasizes that the solute flux is averaged (or upscaled) over A and, hence, its statistics depend on the sampling area A . Note that in following expressions, dependence of the sampling area, A , on \mathbf{y} is understood and will not be stated explicitly. From the solute mass flux we define the *solute discharge* over the sampling area A , $Q [MT^{-1}]$, as

$$Q(t, \mathbf{y}; x, A) = q(t, \mathbf{y}; x, A) A, \quad (11)$$

where $Q(t, \mathbf{y}; x, A)$ quantifies the solute mass crossing A centred at \mathbf{y} at time t . Statistics of Q are readily obtained from statistics of q using (11).

4. Solute flux statistics

During any particular realization of a hypothetical experiment, the *particle* travel time and transverse locations $[\tau(x; \mathbf{a}), \boldsymbol{\eta}(x; \mathbf{a})]$, will vary in a random manner due to the fluctuations in $V(\mathbf{x})$ on all scales. The *plume* travel time and transverse locations $[T(x; A_0), \mathbf{Y}(x; A_0)]$, will vary in an irregular manner resulting from the velocity fluctuations on the scale larger than the plume size; these variations would decrease as the plume size increases. The random quantities $[\theta(x; \mathbf{a}, A_0), \boldsymbol{\mathfrak{A}}(x; \mathbf{a}, A_0)]$ vary in a random manner due to velocity fluctuations on a scale smaller than the plume size. In this section we wish to compute the relative first two moments of solute flux using the statistics of $[\theta(x; A_0, \mathbf{a}), \boldsymbol{\mathfrak{A}}(x; A_0, \mathbf{a})]$, and $[T(x; A_0), \mathbf{Y}(x; A_0)]$.

4.1. Probabilistic model of relative dispersion

The basic probability density functions (p.d.f.s) for describing the transport of a solute plume are

$$\left. \begin{aligned} f_1(\tau - T, \boldsymbol{\eta} - \mathbf{Y}, T, \mathbf{Y}; x, A_0, \mathbf{a}) &\equiv f_1(\theta, \boldsymbol{\mathfrak{A}}, T, \mathbf{Y}; x, A_0, \mathbf{a}), \\ f_2(\tau - T, \tau' - T, \boldsymbol{\eta} - \mathbf{Y}, \boldsymbol{\eta}' - \mathbf{Y}, T, \mathbf{Y}; x, A_0, \mathbf{a}, \mathbf{b}) &\equiv f_2(\theta, \theta', \boldsymbol{\mathfrak{A}}, \boldsymbol{\mathfrak{A}}', T, \mathbf{Y}; x, A_0, \mathbf{a}, \mathbf{b}). \end{aligned} \right\} \quad (12)$$

The p.d.f.s f_1 and f_2 are functions of the location of the CP, x , of the size and shape of the source area, indicated by A_0 , and of the particle initial position \mathbf{a} . The subscript 1 in (12) indicates that the p.d.f. f_1 is based on the statistics of one particle, whereas the subscript 2 indicates that f_2 moments are computed from two particles located at \mathbf{a} and \mathbf{b} . In (12), $\tau = \tau(x; \mathbf{a})$, $\boldsymbol{\eta} = \boldsymbol{\eta}(x; \mathbf{a})$ and $\tau' = \tau(x; \mathbf{b})$, $\boldsymbol{\eta}' = \boldsymbol{\eta}'(x; \mathbf{b})$.

Following the definitions of $\theta = \tau - T$ and $\boldsymbol{\mathfrak{A}} = \boldsymbol{\eta} - \mathbf{Y}$, the basic p.d.f.s describing particle transport in an absolute sense are obtained from (12) as

$$\left. \begin{aligned} f_1(\tau, \boldsymbol{\eta}; x, A_0, \mathbf{a}) &= \int_0^\infty \int_0^\infty f_1(\theta, \boldsymbol{\mathfrak{A}}, T, \mathbf{Y}; x, A_0, \mathbf{a}) dT d\mathbf{Y}, \\ f_2(\tau, \tau', \boldsymbol{\eta}, \boldsymbol{\eta}'; x, A_0, \mathbf{a}, \mathbf{b}) &= \int_0^\infty \int_0^\infty f_2(\theta, \theta', \boldsymbol{\mathfrak{A}}, \boldsymbol{\mathfrak{A}}', T, \mathbf{Y}; x, A_0, \mathbf{a}, \mathbf{b}) dT d\mathbf{Y}, \end{aligned} \right\} \quad (13)$$

Using the theorem on conditional probabilities, (13) can alternatively be written as

$$\left. \begin{aligned} f_1(\tau, \boldsymbol{\eta}; x, A_0, \mathbf{a}) &= \int_0^\infty \int_0^\infty f_1(\theta, \boldsymbol{\mathfrak{A}} | T, \mathbf{Y}; x, A_0, \mathbf{a}) f(T, \mathbf{Y}) dT d\mathbf{Y}, \\ f_2(\tau, \tau', \boldsymbol{\eta}, \boldsymbol{\eta}'; x, A_0, \mathbf{a}, \mathbf{b}) &= \int_0^\infty \int_0^\infty f_2(\theta, \theta', \boldsymbol{\mathfrak{A}}, \boldsymbol{\mathfrak{A}}' | T, \mathbf{Y}; x, A_0, \mathbf{a}, \mathbf{b}) f(T, \mathbf{Y}) dT d\mathbf{Y}, \end{aligned} \right\} \quad (14)$$

where $f_1(\cdot | T, \mathbf{Y})$ and $f_2(\cdot | T, \mathbf{Y})$ are conditional p.d.f.s, and $f(T, \mathbf{Y})$ quantifies plume meandering within the ensemble.

The advection of a plume as a whole is statistically described by the p.d.f. $f(T, \mathbf{Y}; x, A_0)$, which provides information on the degree of uncertainty in the plume position and arrival at the CP. This p.d.f. may be useful for designing the total monitoring network size in the vicinity of potential source areas (e.g. landfills or waste repositories). In addition, $f(T, \mathbf{Y}; x, A_0)$ is the *reducible* uncertainty through measurement conditioning. Collecting measurements at fixed locations or sequentially in stages can be used to condition $f(T, \mathbf{Y}; x, A_0)$ and ultimately reduce the uncertainty in predicting the migration of a plume as a whole.

Our main focus here is to study the effect of sub-plume velocity fluctuations on the mean and variance of the reactive solute mass flux at the CP at x . By setting in (14)

$$f(T, \mathbf{Y}) = \delta(T - \langle \tau \rangle) \delta(\mathbf{Y} - \mathbf{a}_0), \quad (15)$$

where δ denotes the Dirac delta function, we eliminate plume meandering, i.e. we eliminate effects of V fluctuations on a scale larger than the plume size; $\mathbf{a}_0(a_{0x} = 0, a_{0y}, a_{0z})$ is the centroid of A_0 .

Substituting (15) into (14), we obtain

$$\left. \begin{aligned} f_1^r(\tau, \boldsymbol{\eta}; x, A_0, \mathbf{a}) &\equiv \int_0^\infty \int_0^\infty f_1(\theta, \boldsymbol{\mathfrak{G}} | T, \mathbf{Y}; x, A_0, \mathbf{a}) \delta(T - \langle \tau \rangle) \delta(\mathbf{Y} - \mathbf{a}_0) dT d\mathbf{Y} \\ &= f_1(\tau - \langle \tau \rangle, \boldsymbol{\eta} - \mathbf{a}_0 | \langle \tau \rangle, \mathbf{a}_0; x, A_0, \mathbf{a}), \\ f_2^r(\tau, \tau', \boldsymbol{\eta}, \boldsymbol{\eta}'; x, A_0, \mathbf{a}, \mathbf{b}) &\equiv \int_0^\infty \int_0^\infty f_2(\theta, \theta', \boldsymbol{\mathfrak{G}}, \boldsymbol{\mathfrak{G}}' | T, \mathbf{Y}; x, A_0, \mathbf{a}, \mathbf{b}) \\ &\quad \times \delta(T - \langle \tau \rangle) \delta(\mathbf{Y} - \mathbf{a}_0) dT d\mathbf{Y} \\ &= f_2(\tau - \langle \tau \rangle, \tau' - \langle \tau \rangle, \boldsymbol{\eta} - \mathbf{a}_0, \boldsymbol{\eta}' - \mathbf{a}_0 | \langle \tau \rangle, \mathbf{a}_0; x, A_0, \mathbf{a}, \mathbf{b}), \end{aligned} \right\} \quad (16)$$

where we denote with a superscript r the p.d.f.s that specifically quantify relative dispersion. The p.d.f.s f_1^r and f_2^r can in principle be constructed by performing a large number of plume realizations (forming an ensemble), superimposing mean arrival times and displacements at the ensemble mean ($\langle \tau \rangle, \mathbf{a}_0$) and then evaluating one- and two-particle advective transport statistics (see figure 1c).

4.2. Mean and variance

Taking the expected value of q (9) with f_1^r (16) we obtain

$$\langle q(t, \mathbf{x}) \rangle = \frac{1}{A} \int_{A_0} \int_A \int_0^\infty \rho_0(\mathbf{a}) \Gamma(t, \tau) f_1^r(\tau, \mathbf{y}'; x, \mathbf{a}) d\tau d\mathbf{y}' d\mathbf{a}. \quad (17)$$

For simplicity, we omit hereafter explicit dependence on A_0 and A which is to be understood. For a non-reactive solute pulse, with sampling over a point (i.e. $A \rightarrow 0$), we get

$$\langle q(t, \mathbf{x}) \rangle = \int_{A_0} \rho_0(\mathbf{a}) f_1^r(t, \mathbf{y}; x, \mathbf{a}) d\mathbf{a}. \quad (18)$$

The variance of the solute flux is evaluated as

$$\sigma_q^2(t, \mathbf{x}) \equiv \langle q^2 \rangle - \langle q \rangle^2, \quad (19)$$

where

$$\langle q^2(t, \mathbf{x}) \rangle = \frac{1}{A^2} \int_{A_0} \int_{A_0} \rho_0(\mathbf{a}) \rho_0(\mathbf{b}) F(t, \mathbf{y}; x, \mathbf{a}, \mathbf{b}) d\mathbf{a} d\mathbf{b} \quad (20)$$

and

$$F \equiv \int_A \int_A \int_0^\infty \int_0^\infty \Gamma(t, \tau) \Gamma(t, \tau') f_2^r(\tau, \tau', \mathbf{y}', \mathbf{y}''; x, \mathbf{a}, \mathbf{b}) d\tau d\tau' d\mathbf{y}' d\mathbf{y}''.$$

For a non-reactive solute pulse with sampling over a point (i.e. $A \rightarrow 0$), we have

$$\langle q^2(t, \mathbf{x}) \rangle = \int_{A_0} \int_{A_0} \rho_0(\mathbf{a}) \rho_0(\mathbf{b}) f_2^r(t, t, \mathbf{y}, \mathbf{y}; x, \mathbf{a}, \mathbf{b}) d\mathbf{a} d\mathbf{b}. \quad (21)$$

The above expressions for $\langle q \rangle$ and σ_q^2 for reactive and non-reactive solute are analogous in form to the expressions in the absolute dispersion formulation, where f_1^r and f_2^r are substituted by the corresponding p.d.f.s f_1 and f_2 (e.g. Dagan *et al.* 1992; Cvetkovic *et al.* 1992; Andricevic & Cvetkovic 1996).

4.3. Correlation structure

The correlation structure of the solute flux, or discharge, represents a statistical function of potential interest in several applications, such as monitoring network design, measurement conditioning, remediation design, etc. It describes the correlation between two solute particles at different locations in space–time coordinates observed at the CP. Since q and consequently Q are not stationary random functions, we write the covariance between two points in space and time as

$$\langle q(t_1, \mathbf{y}_1; x)q(t_2, \mathbf{y}_2; x) \rangle$$

where the dependence is on t_1, \mathbf{y}_1 and t_2, \mathbf{y}_2 , i.e. on six variables.

Generally it is not possible to use techniques developed for stationary random functions to evaluate the above expression. However, we define the integral form of the above statistical function as

$$P(t^*, \mathbf{y}^*; x) \equiv \int \int \langle q(t, \mathbf{y}; x)q(t + t^*, \mathbf{y} + \mathbf{y}^*; x) \rangle dt d\mathbf{y} / \int \int \sigma_q^2(t, \mathbf{y}; x) dt d\mathbf{y}, \quad (22)$$

where integration is over all time and over the entire control plane at x . The above integral correlation measure depends only on three variables in the three-dimensional case: the temporal lag t^* and the two components of the transverse lag vector \mathbf{y}^* . Furthermore, $P(t^*, \mathbf{y}^*; x)$ is quadrant symmetric (which implies statistical homogeneity in a weak sense, see e.g. Vanmarcke 1983) and is analogous to the distance–neighbour function of Richardson (1926). For the solute flux it behaves like a correlation function. A similar finding for the transverse spreading was reported by Chatwin & Sullivan (1979) in turbulent diffusion experiments at Lake Huron.

The solute flux correlation measure in (22) is a measure of solute flux structure throughout the plume with all parts being given the same weight. For a given temporal lag t^* and spatial lag \mathbf{y}^* , (22) represents the effective correlation measure at x for the entire plume. This correlation measure is based on the relative dispersion solution and provides the actual measure of correlation between two points in a single realization. For example, the correlation scale in the transverse direction can be used as a guideline for transverse spacing between sampling wells at CP and the correlation scale in time can be used as a guideline for sampling frequency of measurements.

4.4. One- and two-particle moments

In the following, we compute the first few moments of the basic p.d.f.s $f_1(\theta, \mathfrak{Z}, T, \mathbf{Y}; x, \mathbf{a})$ and $f_2(\theta, \theta', \mathfrak{Z}, \mathfrak{Z}', T, \mathbf{Y}; x, \mathbf{a}, \mathbf{b})$.

The first moments of f_1 are computed as

$$\left. \begin{aligned} \langle \theta(x; \mathbf{a}) \rangle &= \frac{1}{A_0} \int_{A_0} \langle \Delta\tau(x; \mathbf{a}, \mathbf{a}') \rangle d\mathbf{a}' = 0, \\ \langle \mathfrak{Z}(x; \mathbf{a}) \rangle &= \frac{1}{A_0} \int_{A_0} \langle \Delta\boldsymbol{\eta}(x; \mathbf{a}, \mathbf{a}') \rangle d\mathbf{a}' = \mathbf{a} - \mathbf{a}_0, \\ \langle T(x) \rangle &= \frac{1}{A_0} \int_{A_0} \langle \tau(x; \mathbf{a}') \rangle d\mathbf{a}' = \langle \tau(x) \rangle, \\ \langle \mathbf{Y}(x) \rangle &= \frac{1}{A_0} \int_{A_0} \langle \boldsymbol{\eta}(x; \mathbf{a}') \rangle d\mathbf{a}' = \mathbf{a}_0, \end{aligned} \right\} \quad (23)$$

where $\mathbf{a}_0(a_{0_x} = 0, a_{0_y}, a_{0_z})$ is the centroid of A_0 .

The second moment $\langle \theta^2 \rangle$ is computed as

$$\langle \theta^2(x; \mathbf{a}, A_0) \rangle = \sigma_\tau^2(x) + \sigma_T^2(x; A_0) - 2 \sigma_{\tau T}(x; A_0, \mathbf{a}). \quad (24)$$

In (24), $\sigma_\tau^2(x) \equiv \langle \tau^2 \rangle - \langle \tau \rangle^2$, and $\sigma_T^2(x; A_0)$ is the second moment of the variability in the plume mean travel time (Selroos 1995)

$$\sigma_T^2 \equiv \langle T^2 \rangle - \langle \tau \rangle^2 = \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \sigma_{\tau\tau'}(x; \mathbf{a}, \mathbf{a}') d\mathbf{a} d\mathbf{a}', \quad (25)$$

while $\sigma_{\tau T}$ is the joint moment between T and τ :

$$\sigma_{\tau T} \equiv \langle \tau T \rangle - \langle \tau \rangle^2 = \frac{1}{A_0} \int_{A_0} \sigma_{\tau\tau'}(x; \mathbf{a}, \mathbf{a}') d\mathbf{a}' \quad (26)$$

where $\sigma_{\tau\tau'}(x; \mathbf{a}, \mathbf{b}) \equiv \langle \tau(x; \mathbf{a})\tau(x; \mathbf{b}) \rangle - \langle \tau \rangle^2$ (Cvetkovic *et al.* 1992).

The joint moment $\langle \theta T \rangle$ is computed as

$$\langle \theta T \rangle = \sigma_{\tau T}(x; \mathbf{a}) - \sigma_T^2(x). \quad (27)$$

The corresponding moments for transverse displacement follow from

$$\left. \begin{aligned} \langle \vartheta^2 \rangle &= \sigma_\eta^2(x) + \sigma_Y^2(x; A_0) - 2 \sigma_{\eta Y}(x; \mathbf{a}, A_0), \\ \langle \chi^2 \rangle &= \sigma_\zeta^2(x) + \sigma_Z^2(x; A_0) - 2 \sigma_{\zeta Z}(x; \mathbf{a}, A_0), \\ \langle \vartheta Y \rangle &= \sigma_{\eta Y}(x; \mathbf{a}, A_0) - \sigma_Y^2(x; A_0), \\ \langle \chi Z \rangle &= \sigma_{\zeta Z}(x; \mathbf{a}, A_0) - \sigma_Z^2(x; A_0), \end{aligned} \right\} \quad (28)$$

where $\sigma_\eta^2(x)$ and $\sigma_\zeta^2(x)$ are transverse displacement variances for a single particle, $\sigma_Y^2(x; A_0)$ and $\sigma_Z^2(x; A_0)$ denote variances of the plume mean transverse location at the CP and are computed in analogy to (25), and $\sigma_{\eta Y}(x; A_0, \mathbf{a})$ and $\sigma_{\zeta Z}(x; A_0, \mathbf{a})$ are defined and computed in analogy to $\sigma_{\tau T}$ (26). In (24) and (28) we emphasize the dependence on A_0 since σ_τ^2 , σ_η^2 and σ_ζ^2 are not dependent on A_0 .

The joint moments between θ , T and ϑ , Y are all functions of the joint moment between travel time and transverse displacement $\sigma_{\tau\eta} \equiv \langle \tau\eta \rangle - \langle \tau \rangle \langle \eta \rangle$. It can be shown under fairly general conditions that for statistically stationary flow $\sigma_{\tau\eta} = 0$ (Dagan *et al.* 1992; G. Dagan, unpublished manuscript).

The joint moments between two particles at \mathbf{a} and \mathbf{b} are computed as

$$\langle \theta\theta' \rangle \equiv \langle \theta(x; \mathbf{a})\theta(x; \mathbf{b}) \rangle = \sigma_{\tau\tau'}(x; \mathbf{a}, \mathbf{b}) + \sigma_T^2(x; A_0) - \sigma_{\tau T}(x; A_0, \mathbf{a}) - \sigma_{\tau T}(x; A_0, \mathbf{b}). \quad (29)$$

Similarly the cross-covariance terms for the transverse displacement follow from

$$\langle \vartheta\vartheta' \rangle \equiv \langle \vartheta(x; \mathbf{a})\vartheta(x; \mathbf{b}) \rangle = \sigma_{\eta\eta'}(x; \mathbf{a}, \mathbf{b}) + \sigma_Y^2(x; A_0) - \sigma_{\eta Y}(x; A_0, \mathbf{a}) - \sigma_{\eta Y}(x; A_0, \mathbf{b}), \quad (30)$$

$$\langle \chi\chi' \rangle \equiv \langle \chi(x; \mathbf{a})\chi(x; \mathbf{b}) \rangle = \sigma_{\zeta\zeta'}(x; \mathbf{a}, \mathbf{b}) + \sigma_Z^2(x; A_0) - \sigma_{\zeta Z}(x; A_0, \mathbf{a}) - \sigma_{\zeta Z}(x; A_0, \mathbf{b}). \quad (31)$$

The moments for f_1^r and f_2^r can be obtained via the Monte-Carlo method by generating a large number of realizations of a plume of particles and statistically evaluating their arrival time and transverse displacement at the CP. An alternative approach is to derive analytical solutions using first-order approximations; these approximations will be presented in § 5.

5. Uniform source distribution

We consider here the special case of a reactive solute that is uniformly distributed over the source area, A_0 , i.e. $\rho_0 = M/A_0 = \text{const.}$, where M is the total injected solute mass. In this case, computations of the relative solute flux statistics simplify considerably; these results will be illustrated in §7.

5.1. Mean and variance of solute flux

The expected absolute solute flux (17) is written using (13) as

$$\begin{aligned} \langle q(t, \mathbf{x}) \rangle &= \frac{M}{A} \int_A \int_0^\infty \Gamma(t, \tau) f_1(\tau, \mathbf{y}') d\tau d\mathbf{y}' \\ &= \frac{M}{A} \int_A \int_0^\infty \int \int \Gamma(t, \tau) f_1(\tau - T, \mathbf{y}' - \mathbf{Y}, T, \mathbf{Y}; \mathbf{x}) dT d\mathbf{Y} d\tau d\mathbf{y}', \end{aligned} \quad (32)$$

where

$$f_1(\theta, \mathfrak{g}, T, \mathbf{Y}) = \frac{1}{A_0} \int_{A_0} f_1(\theta, \mathfrak{g}, T, \mathbf{Y}; \mathbf{a}) d\mathbf{a}. \quad (33)$$

The moments of $f_1(\theta, \mathfrak{g}, T, \mathbf{Y})$ (33) can be inspected using the result given in the Appendix; we find that all the joint moments between $\theta, \mathfrak{g}, \chi$ and T, Y, Z are zero, following the definitions of $\theta, \mathfrak{g}, \chi$ (6), i.e.

$$\frac{1}{A_0} \int_{A_0} \langle \theta T \rangle d\mathbf{a} = \frac{1}{A_0} \int_{A_0} \langle \mathfrak{g} Y \rangle d\mathbf{a} = \frac{1}{A_0} \int_{A_0} \langle \mathfrak{g} Z \rangle d\mathbf{a} = \frac{1}{A_0} \int_{A_0} \langle \chi Z \rangle d\mathbf{a} = \dots = 0. \quad (34)$$

Hence we can write

$$f_1(\theta, \mathfrak{g}, T, \mathbf{Y}) = f_1(\theta, \mathfrak{g}) f(T, \mathbf{Y}), \quad (35)$$

which is a statement of independence; $f_1(\theta, \mathfrak{g})$ is a joint p.d.f. for the relative travel time and transverse displacements with $f_1(\theta, \mathfrak{g}, T, \mathbf{Y})$ defined in (33).

Using (35), the p.d.f. $f_1(\tau, \boldsymbol{\eta})$ can be written

$$f_1(\tau, \boldsymbol{\eta}; \mathbf{x}) = \int_0^\infty \int_0^\infty f_1(\tau - T, \boldsymbol{\eta} - \mathbf{Y}) f(T, \mathbf{Y}) dT d\mathbf{Y}, \quad (36)$$

which is a convolution transform of distribution functions with the property that the first and second moments of $f_1(\tau, \boldsymbol{\eta})$ are equal to the summation of corresponding first and second moments of $f_1(\theta, \mathfrak{g})$ and $f(T, \mathbf{Y})$ (e.g. Gifford 1959; Hirshman & Widder 1955). Since the unconditional p.d.f. $f_1(\theta, \mathfrak{g})$ (35) is identical to a conditional p.d.f. $f_1(\theta, \mathfrak{g} | T, \mathbf{Y})$ in view of independence (34), it follows that (36) is a special case of (14).

To remove the plume meandering, we substitute (15) into (36) and obtain the p.d.f. for τ and $\boldsymbol{\eta}$ for relative dispersion which has been averaged over A_0 :

$$f_1^r(\tau, \boldsymbol{\eta}; \mathbf{x}) \equiv f_1(\tau - \langle \tau \rangle, \boldsymbol{\eta} - \mathbf{a}_0; \mathbf{x}, A_0). \quad (37)$$

The mean solute flux is obtained by averaging q (9) using f_1^r (37):

$$\langle q(t, \mathbf{x}) \rangle = \frac{M}{A} \int_0^\infty \Gamma(t, \tau) f_1^r(\tau) d\tau \int_A f_1^r(\mathbf{y}') d\mathbf{y}', \quad (38)$$

where we have also taken advantage of the statistical independence of τ and $\boldsymbol{\eta}$.

The variance of the solute flux is evaluated as

$$\sigma_q^2(t, \mathbf{x}) \equiv \langle q^2 \rangle - \langle q \rangle^2, \quad (39)$$

where

$$\langle q^2(t, \mathbf{x}) \rangle = \left(\frac{M}{A_0 A} \right)^2 \int_{A_0} \int_{A_0} F(t, \mathbf{y}; x, \boldsymbol{\alpha}) d\mathbf{a} d\mathbf{b} \quad (40)$$

and

$$F \equiv \int_0^\infty \int_0^\infty \Gamma(t, \tau) \Gamma(t, \tau') f_2^r(\tau, \tau'; x, \boldsymbol{\alpha}) d\tau d\tau' \int_A \int_A f_2^r(\mathbf{y}, \mathbf{y}'; x, \boldsymbol{\alpha}) d\mathbf{y}' d\mathbf{y}''.$$

In (40), $\boldsymbol{\alpha} = \mathbf{a} - \mathbf{b}$, i.e. the dependence of the joint moments of f_2^r is on the separation, rather than absolute positions \mathbf{a} and \mathbf{b} , in view of statistical stationarity.

The description of relative dispersion for a solute plume requires knowledge of the p.d.f.s f_1^r and f_2^r , or an infinite number of statistical moments. Our approach to this Lagrangian closure problem is to evaluate a finite number of statistical moments and assume certain shapes for f_1^r and f_2^r .

5.2. One- and two-particle-pair moments

In the following, we wish to compute the first few moments of the p.d.f.s $f_1^r(\tau)$ and $f_2^r(\tau, \tau'; \boldsymbol{\alpha})$, and $f_1^r(\boldsymbol{\eta})$ and $f_2^r(\boldsymbol{\eta}, \boldsymbol{\eta}'; \boldsymbol{\alpha})$ which will be used for evaluating the mean and variance of the relative solute mass flux.

The first moment of $f_1^r(\tau)$ is $\langle \tau \rangle$, and of $f_1^r(\boldsymbol{\eta})$ is \mathbf{a}_0 . The second moment of $f_1^r(\tau)$ is denoted by Σ_θ^2 and is evaluated as

$$\begin{aligned} \Sigma_\theta^2(x; A_0) &\equiv \frac{1}{A_0} \int_{A_0} \langle \theta^2(x; \mathbf{a}) \rangle d\mathbf{a} = \frac{1}{2} \int_{A_0} \int_{A_0} \langle [\Delta\tau(x; \mathbf{a}, \mathbf{a}')]^2 \rangle d\mathbf{a} d\mathbf{a}' \\ &= \sigma_\tau^2(x) - \sigma_T^2(x; A_0). \end{aligned} \quad (41)$$

The factor 1/2 in (41) results from the 'two particle' theorem which can be stated as that the mean-square separation of two dispersing particles is just twice their mean-square distance from the centre of mass (e.g. Batchelor 1952; Csanady 1973; Fischer *et al.* 1979). Equation (41) was derived earlier by Selroos (1995), whereas the corresponding expression for spatial moments in aquifers was derived by Kitanidis (1988) and Dagan (1989).

Second moments for transverse displacement p.d.f.s $f_1^r(\boldsymbol{\eta})$ and $f_1^r(\boldsymbol{\zeta})$ follow respectively from

$$\begin{aligned} \Sigma_\theta^2(x) &\equiv \frac{1}{A_0} \int_{A_0} \langle \theta^2(x; \mathbf{a}) \rangle d\mathbf{a} \\ &= \frac{1}{2} \int_{A_0} \int_{A_0} \langle [\Delta\eta]^2 \rangle d\mathbf{a} d\mathbf{a}' = \sigma_\theta^2(0; A_0) + \sigma_\eta^2(x) - \sigma_Y^2(x; A_0), \end{aligned} \quad (42)$$

$$\begin{aligned} \Sigma_\chi^2(x) &= \frac{1}{A_0} \int_{A_0} \langle \chi^2(x; \mathbf{a}) \rangle d\mathbf{a} \\ &= \frac{1}{2} \int_{A_0} \int_{A_0} \langle [\Delta\zeta]^2 \rangle d\mathbf{a} d\mathbf{a}' = \sigma_\chi^2(0; A_0) + \sigma_\zeta^2(x) - \sigma_Z^2(x; A_0), \end{aligned} \quad (43)$$

where $\sigma_\theta^2(0; A_0)$ and $\sigma_\chi^2(0; A_0)$ denote the initial variances in transverse directions due to the finite source size.

Next, we wish to compute the moments of the joint p.d.f.s f_2^r . The first and second moment of $f_2^r(\tau, \tau'; \boldsymbol{\alpha})$ are $\langle \tau \rangle$ and Σ_θ^2 , and of $f_2^r(\boldsymbol{\eta}, \boldsymbol{\eta}'; \boldsymbol{\alpha})$ are \mathbf{a}_0 and Σ_θ^2 . The joint moments are denoted by $\Sigma_{\theta\theta'}(x; \boldsymbol{\alpha})$, $\Sigma_{\theta\theta'}(x; \boldsymbol{\alpha})$, and $\Sigma_{\chi\chi'}(x; \boldsymbol{\alpha})$.

The joint moment for travel time, $\Sigma_{\theta\theta'}(x; \boldsymbol{\alpha})$, consistent with $\Sigma_{\theta}^2(x)$ is obtained by averaging the travel time cross-covariance between two particle-pairs over A_0 . Note that the dependence on $\boldsymbol{\alpha}(\alpha_y, \alpha_z)$ implies the dependence on absolute values of the components, i.e. $\alpha_y = |a_y - b_y|$ and $\alpha_z = |a_z - b_z|$.

In particular, $\Sigma_{\theta\theta'}(x; \boldsymbol{\alpha})$ is defined as the cross-covariance between $\Delta\tau(x; \mathbf{a}, \mathbf{a}')$ and $\Delta\tau'(x; \mathbf{b}, \mathbf{b}')$ integrated over separations between two particle-pairs within A_0 :

$$\Sigma_{\theta\theta'}(x; \boldsymbol{\alpha}) = \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \langle \Delta\tau(x; \mathbf{a}, \mathbf{a}') \Delta\tau'(x; \mathbf{b}, \mathbf{b}') \rangle d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}'). \quad (44)$$

Similarly the cross-covariance terms for the transverse displacement follow from

$$\left. \begin{aligned} \Sigma_{gg'}(x; \boldsymbol{\alpha}) &= \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \langle \Delta\eta(x; \mathbf{a}, \mathbf{a}') \Delta\eta(x; \mathbf{b}, \mathbf{b}') \rangle d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}'), \\ \Sigma_{\zeta\zeta'}(x; \boldsymbol{\alpha}) &= \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \langle \Delta\zeta(x; \mathbf{a}, \mathbf{a}') \Delta\zeta(x; \mathbf{b}, \mathbf{b}') \rangle d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}'). \end{aligned} \right\} \quad (45)$$

The above expressions can be further developed by substituting (7) into (44) and (45), and considering two particle-pairs at $(\mathbf{a}, \mathbf{a}')$ and $(\mathbf{b}, \mathbf{b}')$. Setting the particle-pair separations to be parallel and of equal magnitude, where $\boldsymbol{\alpha} = \mathbf{a} - \mathbf{b} = \mathbf{a}' - \mathbf{b}'$ denotes the separation between the two pairs, and $\boldsymbol{\beta} = \mathbf{a} - \mathbf{a}' = \mathbf{b} - \mathbf{b}'$ the separation within each pair, the integrated cross-covariance, for instance, for the travel time can be written as

$$\begin{aligned} \Sigma_{\theta\theta'}(x; \boldsymbol{\alpha}) &= \frac{1}{2} \sigma_{\tau\tau'}(x; \mathbf{a} - \mathbf{b}) + \frac{1}{2} \sigma_{\tau\tau'}(x; \mathbf{a}' - \mathbf{b}') \\ &\quad - \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \sigma_{\tau\tau'}(x; \mathbf{a} - \mathbf{b}') d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}') \\ &\quad - \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \sigma_{\tau\tau'}(x; \mathbf{b} - \mathbf{a}') d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}') \\ &= \sigma_{\tau\tau'}(x; \boldsymbol{\alpha}) - \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \sigma_{\tau\tau'}(x; \boldsymbol{\alpha} + \boldsymbol{\beta}) d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}') \\ &\quad - \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \sigma_{\tau\tau'}(x; \boldsymbol{\alpha} - \boldsymbol{\beta}) d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}'). \end{aligned} \quad (46)$$

Again, the dependence on vectors implies dependence on absolute values of components, for instance, $\mathbf{b} - \mathbf{a}'$ on $|b_y - a'_y|$ and $|b_z - a'_z|$, $\boldsymbol{\alpha} + \boldsymbol{\beta}$ on $|\alpha_y + \beta_y| = |a_y - b_y + a_y - a'_y|$ and $|\alpha_z + \beta_z| = |a_z - b_z + a_z - a'_z|$, etc. The double integration over A_0 can be simplified to a single integration over the separation $\boldsymbol{\beta}$ within A_0 . In §5, expressions for $\Sigma_{\theta\theta'}$, $\Sigma_{gg'}$ and $\Sigma_{\zeta\zeta'}$ will be fully developed for a square planar source where these simplifications will be apparent. For zero separation between the particle-pairs, we obtain the required relationship

$$\Sigma_{\theta\theta'}(x; A_0, \alpha_y = 0, \alpha_z = 0) = \Sigma_{\theta}^2(x; A_0) = \sigma_{\tau}^2(x) - \sigma_T^2(x; A_0). \quad (47)$$

Expressions similar to (46) and (47) can be written for transverse cross-covariances.

5.3. Bulk measure of solute flux

If non-reactive solute is released as a pulse, $\Gamma(t, \tau) = \delta(t - \tau)$, and sampling is over a point (i.e. $A \rightarrow 0$), then (17) becomes

$$\langle q(t, \mathbf{x}) \rangle = M f_1^r(t, \mathbf{y}; x) \quad (48)$$

i.e. the solute mass flux is proportional to f_1^r . The outstanding feature for solute flux advective transport is the average temporal length of a plume (spreading of breakthrough) and transverse width of a plume. For non-reactive solute, a single measure of this temporal length and transverse width is $\ell_\theta(x; A_0)$ and $\ell_\mathfrak{g}(x; A_0)$, respectively, where

$$\left. \begin{aligned} \ell_\theta(x; A_0) &\equiv \left\{ \frac{1}{M} \int (t - \langle \tau \rangle)^2 \langle q \rangle dt \right\}^{1/2} = \left\{ \int t^2 f_1^r(t; x, A_0) dt \right\}^{1/2} = \Sigma_\theta, \\ \ell_\mathfrak{g}(x; A_0) &\equiv \left\{ \frac{1}{M} \int (\mathbf{y} - \mathbf{a}_0)^2 \langle q \rangle d\mathbf{y} \right\}^{1/2} = \left\{ \int \mathbf{y}^2 f_1^r(\mathbf{y}; x, A_0) d\mathbf{y} \right\}^{1/2} = \Sigma_\mathfrak{g} \end{aligned} \right\} \quad (49)$$

and $\ell_\mathfrak{g} = [\ell_\eta, \ell_\zeta]$. As a consequence of mass conservation, the magnitude of the mean non-reactive solute flux is of the order $(M/\ell_\theta \ell_\eta \ell_\zeta)$ for the bulk of the plume at the CP.

6. First-order results

The hydraulic conductivity, K , is assumed to be a statistically stationary random space function, log-normally distributed, i.e. $K = K_g \exp(k)$, where $k : N(0, \sigma_k^2)$, K_g is the geometric mean, σ_k^2 is the log-hydraulic conductivity variance, and k is spatially correlated following a negative exponential function with the integral scale I . The resulting velocity field in the aquifer, $\mathbf{V}(\mathbf{x})$, is also a statistically stationary random space function assumed to be steady with the mean hydraulic gradient parallel to the x -coordinate axis. The injection plane set at the origin, $x = 0$, is assumed for simplicity as a square, $A_0 = H \times H$. In the following, we focus on computing Σ_θ^2 , $\Sigma_\mathfrak{g}^2$, $\Sigma_{\theta\theta'}$ and $\Sigma_{\mathfrak{g}\mathfrak{g}'}$ which will be used for illustration of results.

6.1. Computation of Σ_θ^2 and $\Sigma_\mathfrak{g}^2$

To evaluate the second moments required for relative p.d.f. f_1^r , we employ the first-order approximation in the velocity field which is based on the assumption that the streamlines do not deviate significantly from the mean fluid direction (e.g. Dagan 1984; Dagan *et al.* 1992). Expanding (1) and (3) we get at first-order

$$\tau(x; \mathbf{a}) = \int_0^x \left[\frac{1}{U} - \frac{u_x(\xi, a_y, a_z)}{U^2} \right] d\xi, \quad (50)$$

$$\eta(x; \mathbf{a}) = \int_0^x \frac{u_y(\xi, a_y, a_z)}{U} d\xi, \quad (51)$$

$$\zeta(x; \mathbf{a}) = \int_0^x \frac{u_z(\xi, a_y, a_z)}{U} d\xi, \quad (52)$$

where $u_i(x, a_y, a_z)$ is the velocity fluctuation in the i -direction, and the first-order approximation of the expansion $(1 + u_x/U)^{-1}$ is used, i.e. $(1 + u_x/U)^{-1} \approx (1 - u_x/U)$. Thus, the travel time difference between two particles follows from

$$\Delta\tau(x; \mathbf{a}, \mathbf{a}') = \frac{1}{U^2} \int_0^x u_x(\xi, a'_y, a'_z) d\xi - \frac{1}{U^2} \int_0^x u_x(\xi, a_y, a_z) d\xi. \quad (53)$$

The second moment for the relative travel time of a plume of particles, for a planar

source of size $A_0 = H \times H$, follows from (24):

$$\begin{aligned}\Sigma_{\theta}^2(x; H) &= \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \langle [\Delta\tau(x; \mathbf{a}, \mathbf{a}')]^2 \rangle d\mathbf{a} d\mathbf{a}' = \sigma_{\tau}^2(x) - \sigma_T^2(x; H) \\ &= \frac{2}{U^2} \int_0^x (x - \xi) C_{u_x}(\xi, 0, 0) d\xi \\ &\quad - \frac{8}{H^4 U^2} \int_0^H \int_0^H \int_0^x (H - \alpha_y)(H - \alpha_z)(x - \xi) C_{u_x}(\xi, \alpha_y, \alpha_z) d\xi d\alpha_y d\alpha_z, \quad (54)\end{aligned}$$

where $\alpha_y \equiv |a_y - a'_y|$, $\alpha_z \equiv |a_z - a'_z|$, and C_{u_x} is the covariance function of the normalized fluid velocity u_x/U , available in a closed form (e.g. Rubin & Dagan 1992).

Similarly for transverse displacements, the separation between two particles follows from

$$\Delta\eta(x; \mathbf{a}, \mathbf{a}') = \int_0^x \frac{u_y(\xi, a_y, a_z)}{U} d\xi - \int_0^x \frac{u_y(\xi, a'_y, a'_z)}{U} d\xi, \quad (55)$$

$$\Delta\zeta(x; \mathbf{a}, \mathbf{a}') = \int_0^x \frac{u_z(\xi, a_y, a_z)}{U} d\xi - \int_0^x \frac{u_z(\xi, a'_y, a'_z)}{U} d\xi. \quad (56)$$

The second moment follows from

$$\begin{aligned}\Sigma_{\eta}^2(x; H) &= \sigma_{\eta}^2(0; H) + 2 \int_0^x (x - \xi) C_{u_y}(\xi, 0, 0) d\xi \\ &\quad - \frac{8}{H^4} \int_0^H \int_0^H \int_0^x (H - \alpha_y)(H - \alpha_z)(x - \xi) C_{u_y}(\xi, \alpha_y, \alpha_z) d\xi d\alpha_y d\alpha_z, \quad (57)\end{aligned}$$

$$\begin{aligned}\Sigma_{\zeta}^2(x; H) &= \sigma_{\zeta}^2(0; H) + 2 \int_0^x (x - \xi) C_{u_z}(\xi, 0, 0) d\xi \\ &\quad - \frac{8}{H^4} \int_0^H \int_0^H \int_0^x (H - \alpha_y)(H - \alpha_z)(x - \xi) C_{u_z}(\xi, \alpha_y, \alpha_z) d\xi d\alpha_y d\alpha_z, \quad (58)\end{aligned}$$

where C_{u_y} and C_{u_z} denote the covariance functions of the normalized fluctuations u_y/U and u_z/U , respectively.

Plume meandering (advection of the plume as a whole) is described by the second term on the right-hand side in (54) for travel time, and by the third term in (57) and (58) for transverse displacements. These terms constitute the second moment of $f(T, Y; x)$ and in conjunction with the ensemble mean can be used to hypothesize the shape of $f(T, Y; x)$.

6.2. Computation of $\Sigma_{\theta\theta'}$ and $\Sigma_{\eta\eta'}$

For the travel time joint p.d.f., f_2^t , we need to evaluate the cross-covariance term between two pairs of particles using the travel time differences $\Delta\tau(x; \mathbf{a}, \mathbf{a}')$ and $\Delta\tau'(x; \mathbf{b}, \mathbf{b}')$. From (29) and (53) we have

$$\begin{aligned}\Sigma_{\theta\theta'} &= \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \langle \Delta\tau(x; \mathbf{a}, \mathbf{a}') \Delta\tau(x; \mathbf{b}, \mathbf{b}') \rangle d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}') \\ &= \frac{1}{2} \frac{1}{A_0^2} \int_{A_0} \int_{A_0} \frac{1}{U^4} \int_0^x \int_0^x \{ \langle u_x(\xi, a_y, a_z) u_x(\xi', b_y, b_z) \rangle \\ &\quad - \langle u_x(\xi, a'_y, a'_z) u_x(\xi', b_y, b_z) \rangle - \langle u_x(\xi, a_y, a_z) u_x(\xi', b'_y, b'_z) \rangle \\ &\quad + \langle u_x(\xi, a'_y, a'_z) u_x(\xi', b'_y, b'_z) \rangle \} d\xi d\xi' d(\mathbf{a} - \mathbf{a}') d(\mathbf{b} - \mathbf{b}'). \quad (59)\end{aligned}$$

Considering again a planar source of size $A_0 = H \times H$, (59) reduces to

$$\begin{aligned} \Sigma_{\theta\theta'}(x; H, \boldsymbol{\alpha}) &= \frac{2}{U^2} \int_0^x (x - \xi) C_{u_x}(\xi, \alpha_y, \alpha_z) d\xi \\ &\quad - \frac{4}{U^2 H^4} \int_0^H \int_0^H \int_0^x (H - \beta_y)(H - \beta_z)(x - \xi) C_{u_x}(\xi, \alpha_y + \beta_y, \alpha_z + \beta_z) d\xi d\beta_y d\beta_z \\ &\quad - \frac{4}{U^2 H^4} \int_0^H \int_0^H \int_0^x (H - \beta_y)(H - \beta_z)(x - \xi) C_{u_x}(\xi, \alpha_y - \beta_y, \alpha_z - \beta_z) d\xi d\beta_y d\beta_z, \end{aligned} \quad (60)$$

where $\boldsymbol{\alpha}(\alpha_y, \alpha_z)$ denotes the separation vector between two particle-pairs and $\boldsymbol{\beta}(\beta_y, \beta_z)$ denotes the separation vector between particles within each pair, respectively.

Similarly for transverse displacement, the cross-covariance terms required for evaluating the transverse joint p.d.f. follow from

$$\begin{aligned} \Sigma_{\theta\theta'}(x; H, \boldsymbol{\alpha}) &= 2 \int_0^x (x - \xi) C_{u_y}(\xi, \alpha_y, \alpha_z) d\xi \\ &\quad - \frac{4}{H^4} \int_0^H \int_0^H \int_0^x (H - \beta_y)(H - \beta_z)(x - \xi) C_{u_y}(\xi, \alpha_y + \beta_y, \alpha_z + \beta_z) d\xi d\beta_y d\beta_z \\ &\quad - \frac{4}{H^4} \int_0^H \int_0^H \int_0^x (H - \beta_y)(H - \beta_z)(x - \xi) C_{u_y}(\xi, \alpha_y - \beta_y, \alpha_z - \beta_z) d\xi d\beta_y d\beta_z \end{aligned} \quad (61)$$

$$\begin{aligned} \Sigma_{\gamma\gamma'}(x; H, \boldsymbol{\alpha}) &= 2 \int_0^x (x - \xi) C_{u_z}(\xi, \alpha_y, \alpha_z) d\xi \\ &\quad - \frac{4}{H^4} \int_0^H \int_0^H \int_0^x (H - \beta_y)(H - \beta_z)(x - \xi) C_{u_z}(\xi, \alpha_y + \beta_y, \alpha_z + \beta_z) d\xi d\beta_y d\beta_z \\ &\quad - \frac{4}{H^4} \int_0^H \int_0^H \int_0^x (H - \beta_y)(H - \beta_z)(x - \xi) C_{u_z}(\xi, \alpha_y - \beta_y, \alpha_z - \beta_z) d\xi d\beta_y d\beta_z. \end{aligned} \quad (62)$$

7. Illustration examples

For illustration purposes we consider a two-dimensional aquifer with transport of non-reactive and reactive solute. In all cases the source is a line of length H at $x = 0$ and a control plane (line) is set at $x = L$; both H and L are normalized with the log-hydraulic conductivity integral scale, I . The mean solute flux and solute flux standard deviation are computed as functions of time and transverse displacement at the control plane. The sampling line, denoted by B , is also normalized with I , and represents an averaging window at the control plane. We assume complete mixing within B as is usually the case in practice when sampling contaminants in aquifers.

Taking again advantage of $\langle \tau \eta \rangle = 0$, we write the p.d.f.s f_1^r and f_2^r as

$$\begin{aligned} f_1^r(\tau, \eta; x) &= f_1^r(\tau; x) f_1^r(\eta; x), \\ f_2^r(\tau, \tau', \eta, \eta'; x, \alpha_y) &= f_2^r(\tau, \tau'; x, \alpha_y) f_2^r(\eta, \eta'; x, \alpha_y). \end{aligned}$$

The mean solute flux defined in (38) is proportional to $f_1^r(\tau; x, A_0)$, assumed to follow a log-normal shape with arithmetic moments $f_1^r(\tau; x) = LN[\langle \tau \rangle = x/U, \Sigma_\theta^2]$, and to $f_1^r(\eta; x) = N[0, \Sigma_\theta^2]$ which is assumed to follow a Gaussian distribution. The assumptions of a Gaussian distribution for η and log-normal for τ are consistent with results from numerical simulations (e.g. Bellin, Saladin & Rinaldo 1992; Cvetkovic, Cheng & Wen 1996). A Gaussian distribution for transverse particle displacement

is also consistent with observations in atmospheric turbulent diffusion (e.g. Csanady 1973; Chatwin & Sullivan 1990). For computing the solute flux variance we hypothesize a joint log-normal p.d.f. for $f_2^r(\tau, \tau'; x, H, \alpha_y)$ and joint Gaussian p.d.f. for $f_2^r(\eta, \eta'; x, H, \alpha_y)$, evaluated with two-dimensional forms of (60) and (61). The above choice of distributions is only for illustrative purposes; other distributions, that are consistent with numerical simulations or field experiments, could be used as alternatives.

7.1. Non-reactive case

For non-reactive solute injected over a line source of extent H , with $\rho_0 = \text{const.}$ [M/L^{-1}], and a sampling window of length B centred at y , the mean solute flux reduces from (38) to

$$\langle q(t, x, y) \rangle = \frac{M}{B} f_1^r(t; x, H) \int_B f_1^r(y'; x, H) dy'. \quad (63)$$

The solute flux variance is $\sigma_q^2(t, x, y) = \langle q^2 \rangle - \langle q \rangle^2$ where (40) reduces to

$$\langle q^2(t, x, y) \rangle = \frac{M^2}{H^2 B^2} \int_H \int_H \int_B \int_B f_2^r(t, t; x, H, \alpha_y) f_2^r(y', y''; x, H, \alpha_y) dy' dy'' da_y da'_y \quad (64)$$

where $\alpha_y = |a_y - a'_y|$ is a separation between two particle pairs, and $M = \rho_0 H$.

We first analyse relative dispersion for the solute discharge across the entire CP, Q , obtained from (11) for $A \rightarrow \infty$ (or $B \rightarrow \infty$); thus only the marginal p.d.f. $f_1^r(t; x, H)$ is required.

Figure 3 shows the first two moments of the solute discharge with $\sigma_k^2 = 0.5$ and the CP set at $20I$ from the source. Figures 3(a) and 3(b) describe the difference between the absolute and relative dispersion for the mean solute discharge and the solute discharge standard deviation, respectively. The two descriptions of the dispersion process converge for a larger source size with a faster convergence for the first (e.g. $H > 10$) than second moment (e.g. $H > 20$) of solute discharge. This indicates that the ergodicity in the mean is reached more rapidly than ergodicity in the second moment of solute discharge. In the limit $H \rightarrow \infty$ equations (54) and (60) reduce to their absolute dispersion results (Cvetkovic *et al.* 1992). In the limit $H \rightarrow 0$, (54) and (60) approach zero, indicating that the relative dispersion does not exist for a point source and transport is described as meandering only.

Figure 4 shows the mean and standard deviation of the solute flux as a function of travel time and transverse displacement at the CP placed at $20I$. The plume mean location at the CP is positioned on the ensemble mean travel time $\langle \tau \rangle$ and transverse displacement $a_0 = 0$ to represent the relative spreading due to the velocity fluctuations on the scale smaller than the plume size. The velocity fluctuations on the scale larger than plume size contribute to the plume meandering and they are removed from the relative solute flux formulation. The relative plume spreading displayed on figure 4 provides important information for a certain class of environmental applications, in particular for the risk assessment where actual concentration fluctuations cause potential harm to humans, etc. Including the plume meandering in the overall ensemble would flatten the contaminant breakthrough, reduce the peak (figure 1b), and consequently would underestimate the potential risk.

The uncertainty in the description of a plume centroid location is a consequence of our inability to precisely estimate where the plume as a whole will migrate due to the larger heterogeneity scale present in aquifers; it is of interest for some applications, for

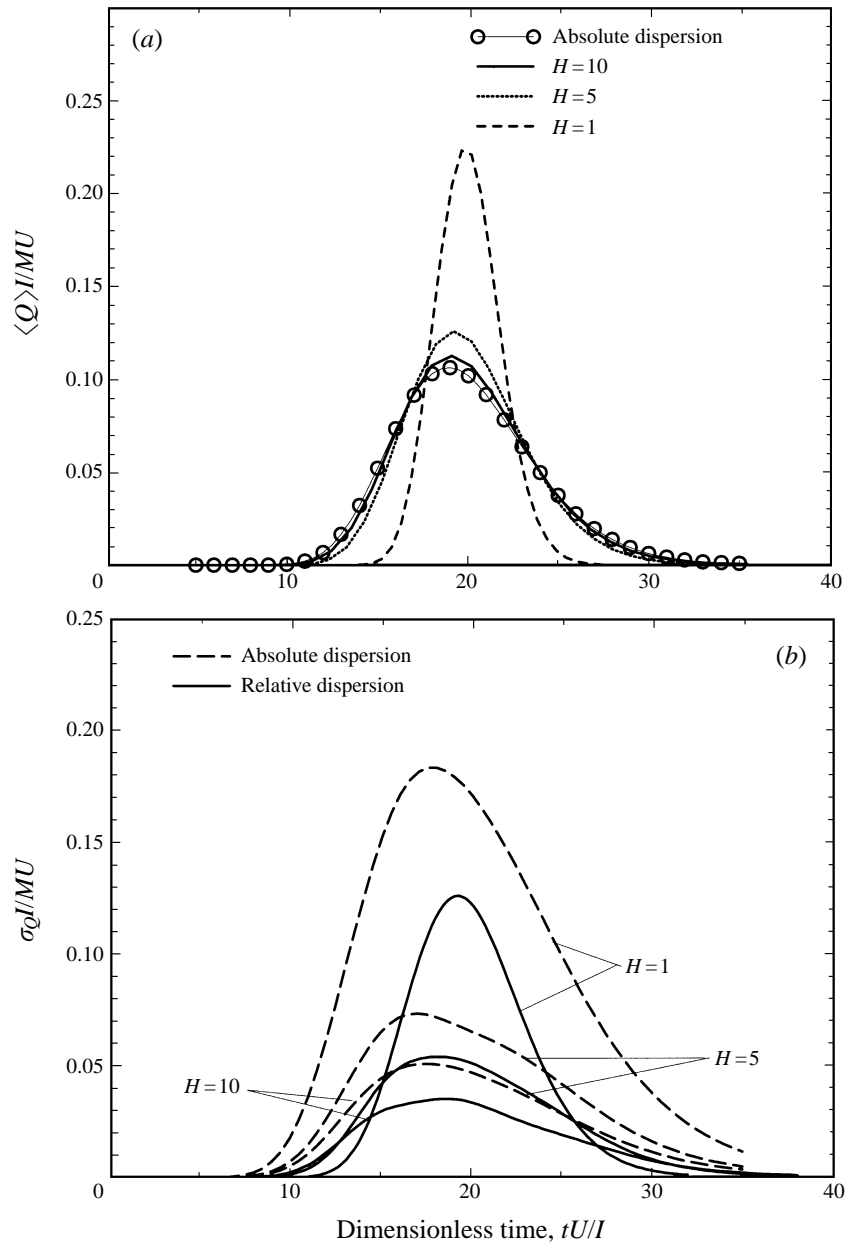


FIGURE 3. Comparison between absolute and relative dispersion formulation for integrated non-reactive solute flux at $x = 20I$: (a) mean solute flux, (b) solute flux standard deviation.

instance, when determining the total monitoring network size and the total number of wells needed to detect a migrating plume. Thus, both relative and absolute dispersion characteristics of subsurface transport are important for some but usually different objectives and, therefore, should be evaluated separately.

To better grasp features of relative dispersion in two dimensional transport, figure 5 displays the travel time and transverse displacement profiles sliced at the plume centreline and at the peak travel time, respectively. In addition, three different

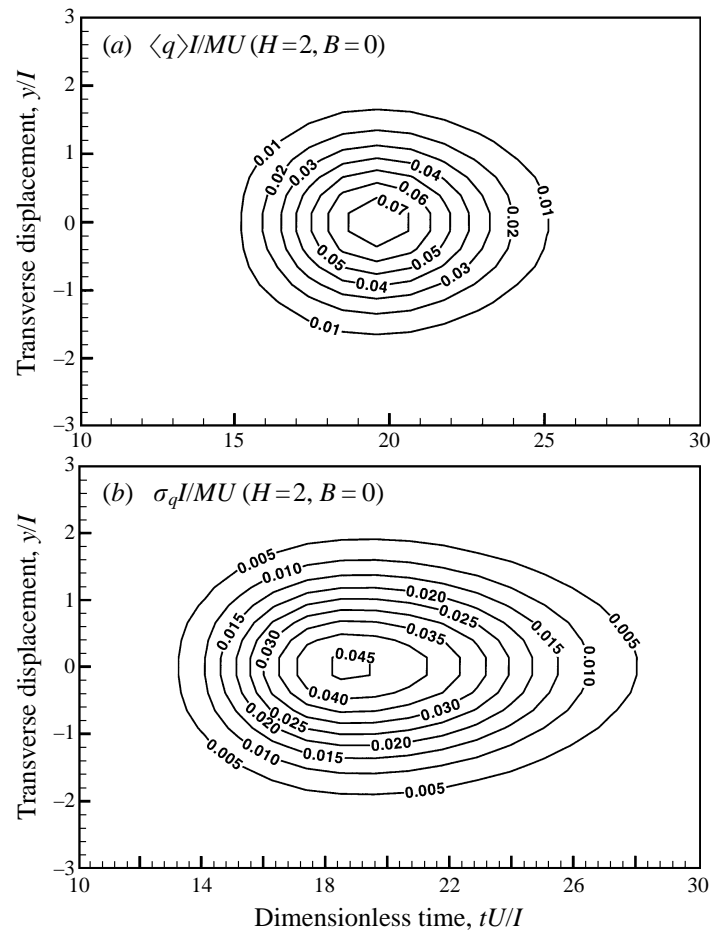


FIGURE 4. Non-reactive solute flux solution as a space-time process ($x = 20I, H = 2, B = 0$):
(a) mean, (b) standard deviation.

sampling detection areas are considered. Larger detection areas cause more flatness in the solute flux distribution in the transverse which is particularly emphasized in the solute flux second moment. For a decreasing sampling size, i.e. $B \rightarrow 0$, the 'point' detection of the solute flux is obtained, say at the Darcy scale approximately 10^{-1} m. The effects of instrument smoothing are expected to be more pronounced for higher moments since high fluctuations, which make an increasingly large contribution for larger moments, are smoothed out. Thus, the sampling area B acts as a moving average window on the solute flux solution for $B = 0$. Evaluation of solute flux statistics, subject to a sampling volume, is necessary for proper measurement conditioning (Andričević 1996).

We also find that the sampling/detection length has a unique scaling effect on the solute flux variance at the plume centre when expressed as a function of the ratio between sampling window and source size, i.e. B/H . This behaviour is presented on figure 5(c) and is independent of the distance to the control plane. The universal scaling effect on figure 5(c) can be used to evaluate the reduction in the solute flux second moment as a result of sampling volume.

In aquifers, the concentration measurements are usually performed *in-situ* using

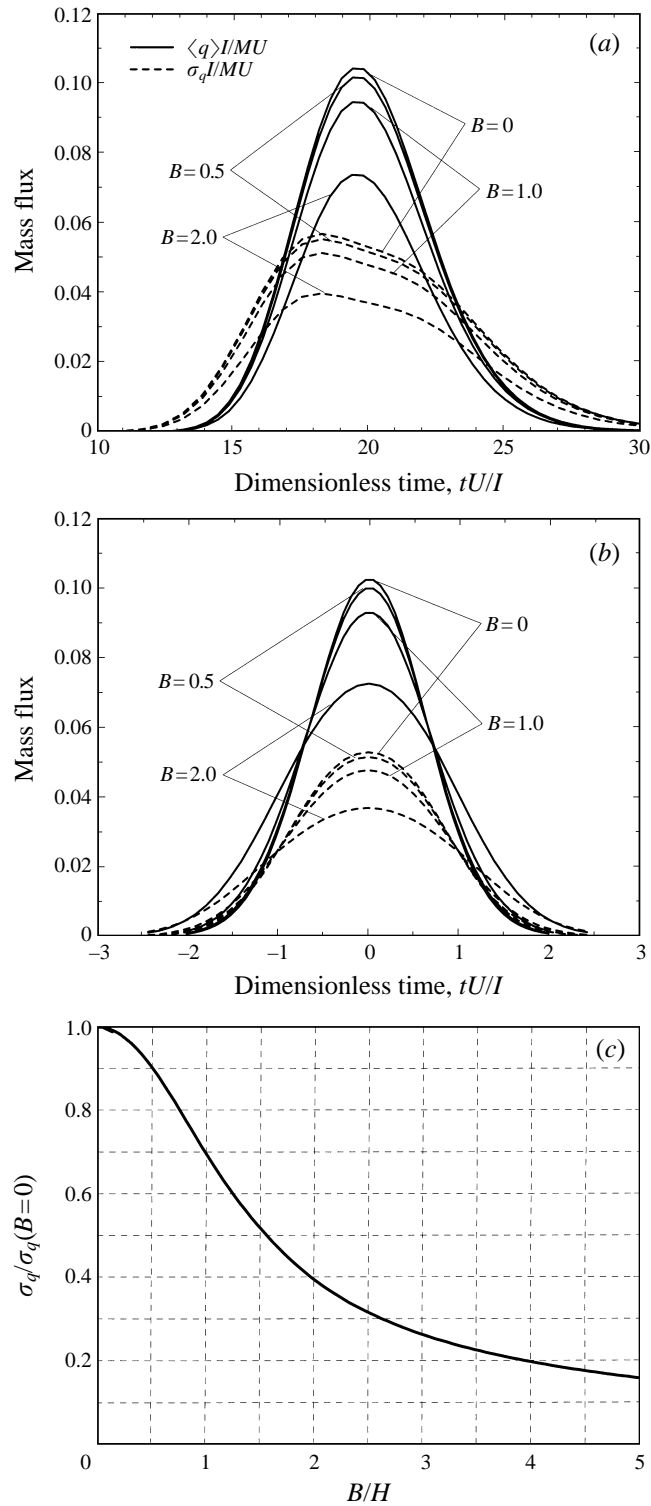


FIGURE 5. Non-reactive solute flux solution for different sampling volumes, (a) mean vs. time for $y/I = 0$, (b) standard deviation vs. transverse displacement for travel time $tU/I = 20$, (c) unique scaling effect of the solute flux variance at the plume centre.

well probes or by withdrawal of water by pumping. In either case, and particularly in the latter, the volume of sampled aquifer is much larger than the pore scale and, therefore, complete mixing within the detection volume due to the sampling will occur. This sampling practice in aquifers acts as instrument smoothing and does not allow detection of possible high solute fluctuations concentrated in the flow paths on a scale smaller than B . The effect of instrument smoothing is to drastically reduce the magnitude of solute flux higher-order moments. If additional temporal sampling time is introduced (e.g. Destouni & Graham 1997), further smoothing would occur.

Although pore-scale dispersion will reduce the concentration fluctuations after advective transport has developed (i.e. the plume is stretched and distorted creating more surface area where pore-scale dispersion can occur), the quantification and verification of its impact on concentration fluctuations from measurements in aquifers is very difficult. Thus, the influence of pore-scale dispersion, if included in modelling, usually cannot be supported by measurement in the subsurface; it thus remains difficult to assess what is the actual pore-scale dispersion effect on the solute transport. However, a finite sampling area A and the pore-scale dispersion yield similar effects on concentration fluctuations, namely they both introduce concentration smoothing and reduce higher-order moments.

7.2. Effect of non-equilibrium sorption

For cases where solute is subject to equilibrium or non-equilibrium mass transfer reactions between the fluid phase and surrounding material, the form of the time retention function needs to be specified. If the migrating solute undergoes a sorption-desorption reaction controlled by first-order kinetics with

$$\psi_m = -\alpha(K_d C - N) - k_0 C, \quad \psi_{im} = \alpha(K_d C - N) - k_0 N \quad (65)$$

the time retention function is (e.g. Cvetkovic & Dagan 1994)

$$\begin{aligned} \gamma(t, \tau) = & \exp[-(\alpha K_d + k_0)t] \delta(t - \tau) + \alpha^2 K_d \tau \exp(-\alpha K_d \tau - \alpha t + \alpha \tau - k_0 t) \\ & \times \tilde{I}_1[\alpha^2 K_d \tau(t - \tau)] H(t - \tau) \end{aligned} \quad (66)$$

where $\tilde{I}_1(z) \equiv I_1(2z^{1/2})/z^{1/2}$ with I_1 being the modified Bessel function of the first kind of order one, α 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 accounts for irreversible mass transfer (degradation in both mobile and immobile phases, or decay). For $\alpha \rightarrow \infty$, reversible mass transfer is under equilibrium conditions, and (66) reduces to $\gamma = e^{-k_0 t} \delta[t - (1 + K_d)\tau]$.

Using (38) and (40), the first two moments of the solute flux are obtained as

$$\langle q(t, x, y) \rangle = \frac{M}{B} \int_B \int_0^\infty \gamma(t, \tau) f_1^r(\tau; x) f_1^r(y'; x) d\tau dy' \quad (67)$$

and $\sigma_q^2(t, x, y) = \langle q^2 \rangle - \langle q \rangle^2$, where

$$\begin{aligned} \langle q^2(t, x, y) \rangle = & \frac{M^2}{H^2 B^2} \int_H \int_H \int_B \int_B \int_0^\infty \int_0^\infty \gamma(t, \tau) \gamma(t, \tau') \\ & \times f_2^r(\tau, \tau'; x, H, \alpha_y) f_2^r(y', y''; x, H, \alpha_y) d\tau d\tau' dy' dy'' da_y da'_y \end{aligned} \quad (68)$$

with $\alpha_y = |a_y - a'_y|$.

Figure 6 shows the solute plume undergoing mass transfer processes with $\alpha^* \equiv \alpha I/U = 0.1$ and $K_d = 1$, displayed in the two-dimensional transport coordinates,

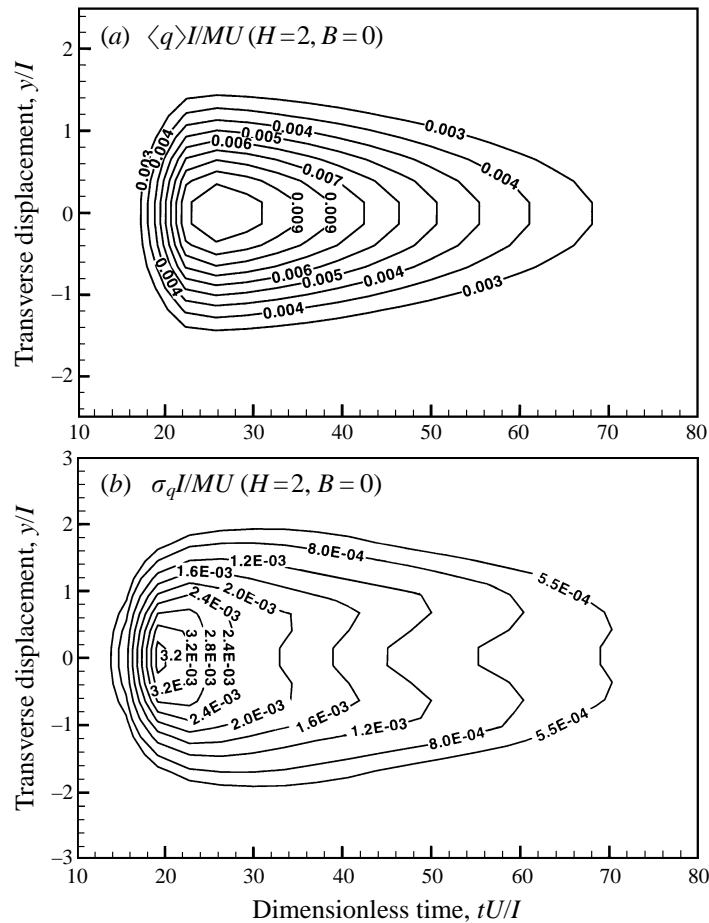


FIGURE 6. Reactive solute flux solution as a space-time process at $CP = 20I$ with $\alpha^* = 0.1$:
(a) mean, (b) standard deviation.

travel time and transverse displacement at x . The effect of tailing due to the mass transfer and time retention is apparent. For larger travel time the plume becomes narrow and may still be present at the CP in measurable quantities. The actual magnitude of this presence is determined by K_d and α^* values. The solute flux standard deviation (figure 6b) shows the development of the bi-modal form of the transversal standard deviation. During the early (rising) part of the breakthrough, the mean and standard deviation of the solute flux are of similar magnitude and σ_q shows a uni-modal distribution. For the later stage of the breakthrough (recession part), the solute flux standard deviation has a dual peak structure which is smoothed out in the high tail values of travel time. This off-centre peak for σ_q is located around $y/I = 0.6$ which corresponds to the highest slope of the mean solute flux distribution.

The effect induced by slow mass transfer (slow compared to the advective transport time) is displayed on figure 7 for the first two moments of the solute flux as a function of time and transverse displacement by slicing figure 6 along the plume centreline and time equal to 20. Since the reaction process is reflected as a time retention mechanism, the important mass transfer effects can be seen from the solute flux as a function of time.

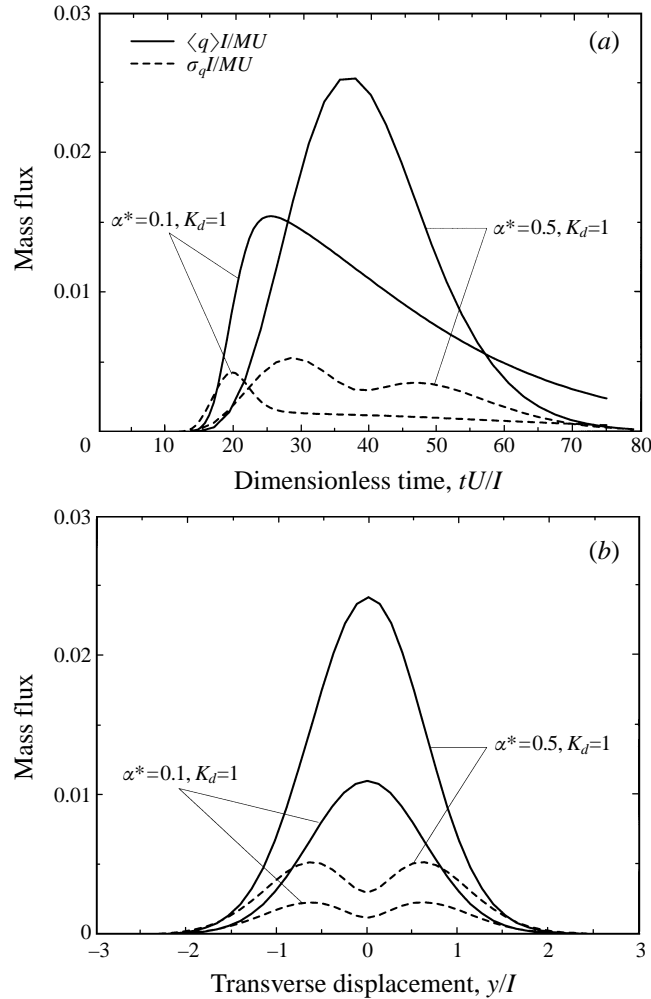


FIGURE 7. Reactive solute flux solution for different mass transfer rates: (a) mass flux vs. travel time for $y/I = 0$, (b) mass flux vs. transverse displacement for travel time $tU/I = 20$.

The transition from the non-reactive case to the reactive one is manifested as a reduction in the solute flux peak and an introduction of the tailing effect. For faster reactions (larger α^*), the peak is shifted in time and increased while tailing diminishes; for sufficiently large α^* (by $\alpha^* > 1$), the local equilibrium assumption (LEA) may be applicable. The contaminant transport solution then behaves as a linear equilibrium where the velocity, and consequently the travel time, is scaled by the retardation factor $1 + K_d$. This can be seen by comparing the mean solute flux from figure 5 ($B = 0$) and figure 7 ($\alpha^* = 0.5$).

7.3. Correlation structure

In figure 8 we present the two-dimensional solute flux integral correlation measure $P(t^*, y^*; x, B)$ (22) for $H = 2, B = 0$. The temporal and transverse lags are presented dimensionless. In terms of comparing correlation structures in space and time an appropriate normalization length is required. Commonly we choose the correlation

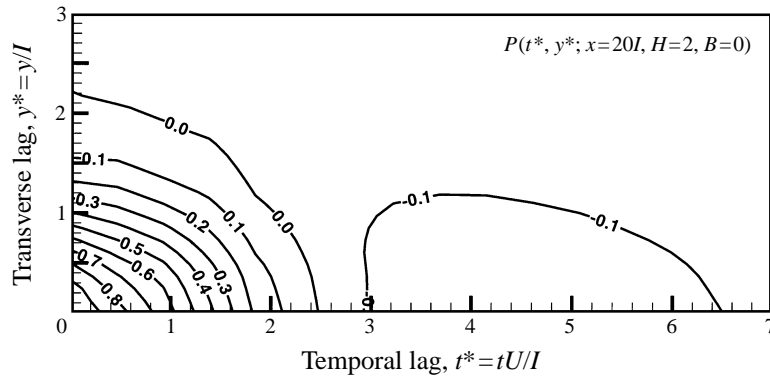


FIGURE 8. Non-reactive solute flux integral correlation measure $P(t^*, y^*; x, B = 0, H = 2)$.

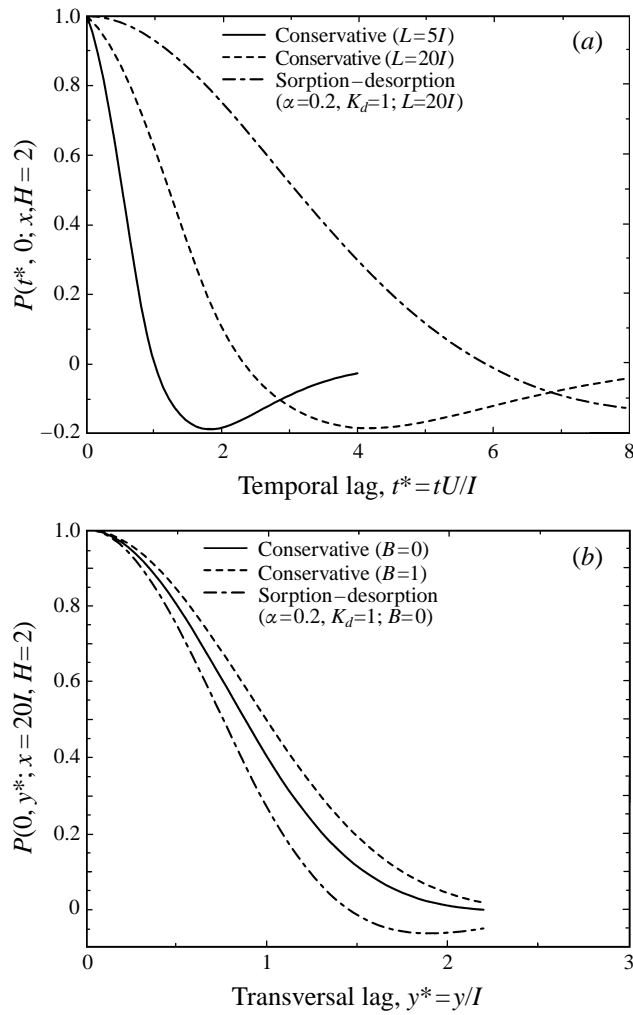


FIGURE 9. Non-reactive solute flux integral correlation measure for different sampling volumes: (a) $P(t^*, 0; x, B, H = 2)$, (b) $P(0, y^*; x, B, H = 2)$.

scale defined as the distance for the e^{-1} decrease of the correlation. Only in the case of a negative exponential type of correlation function is the correlation scale the same as the integral scale, the latter defined as the integral of the correlation function normalized with the variance. Figure 8 shows the correlation scale in the transverse coordinate to be around I and $1.5I$ for travel time. In words, two solute particles in a single realization crossing the CP at the same time ($t^* = 0$) are correlated within the distance of I and similarly two solute particles crossing the CP at the same location ($y^* = 0$) will be correlated in time within $1.5I$. These two correlation measures may provide useful guidelines for designing sampling networks in the subsurface. Any other correlation depending on both temporal and transverse lags can be deduced from figure 8.

Figure 9 shows a different sensitivity analysis of correlation measures of the solute flux by keeping one coordinate lag equal to zero, i.e. the correlation measure along the plume centreline (figure 9a displays $P(t^*, 0; x, B)$) and transverse cross-section at $t = \langle \tau \rangle$ (figure 9b displays $P(0, y^*; x, B)$). Figure 9(a) depicts the development of the temporal correlation scale for the CP located at $5I$ and $20I$ with a clear increase of the correlation scale at the larger distance from the source. If, in addition, the solute undergoes a sorption–desorption reaction, the temporal correlation is further increased. That transverse correlation scale of the plume, $P(0, y^*; x, B)$, on figure 9(b) shows an increase in the transverse correlation by considering the sampling detection ($B = 1$); however, when sorption–desorption is active, the transverse correlation scale is reduced compared to ‘point’ detection. The tailing effect (figure 6) causes a narrow plume which is the reason why the transverse correlation scale on figure 9(b) is reduced. In all cases there is a smooth Gaussian-type correlation structure for the transverse direction while the temporal correlation has a region of negative correlation and behaves like a hole-Gaussian-type correlation function.

8. Summary

Relative dispersion of the mass flux for non-reactive and reactive solute is presented in terms of the first two moments, i.e. mean solute flux and solute flux variance. The mean solute flux is described as a space–time process where time refers to the solute flux breakthrough and space refers to the transverse displacement distribution at the control plane placed perpendicular to the mean flow direction. The statistical moments for describing the mean solute flux distribution are derived using the statistics of a single particle pair while moments for the distribution of the solute flux variance are based on the motion of two particle pairs. Statistics of the solute flux, as a space–time process, fully describe the evolution of a contaminant plume in heterogeneous aquifers.

The results indicate that the relative dispersion of the solute flux approaches the absolute dispersion when source size is increased. This convergence is faster in the mean than in the standard deviation of the solute flux. For a decreasing source size, the difference between the absolute and relative dispersion formulations increases. The smoothing effect due to a finite sampling area influences the first two moments of the solute flux. This influence is more pronounced in the solute flux second-moment distribution by reducing the peak with enhanced spreading in space and time. The solute flux solution for contaminants undergoing a sorption reaction shows the effect of tailing in arrival time with a bi-modal transverse distribution of the solute flux second moment in the recession stage of the breakthrough.

The integrated correlation structure of the solute flux in (22) has been derived as an effective, global space–time measure of the migrating plume. When evaluated for a

fixed time, this correlation describes the probability that two points at the CP are in the marked fluid and as such is a potentially useful indicator for optimizing spacing of sampling locations in aquifers. Conversely, when evaluated for a fixed point at the CP, P describes the temporal correlation of the breakthrough and can be used to assign the frequency of measurements.

The derived integral-form solution for the solute flux moments neglects the effect of pore-scale dispersion. Pore-scale dispersion is due to velocity fluctuations on the scale of the order of say 10^{-3} m, whereas the solute flux solution is based on the flow field evaluated from hydraulic data assumed to have been sampled on (or downscaled to) the Darcy scale, of the order of say 10^{-1} m. The pore-scale dispersion effect is known to increase with transport time and affects most the solute flux higher moments. Its maximum impact is anticipated for point measurements (i.e. for $A \rightarrow 0$) which is approximately on the Darcy scale (e.g. Graham & McLaughlin 1989; Li & McLaughlin 1991; Kapoor & Gelhar 1994; Zhang & Neuman 1996; Dagan & Fiori 1997). In many applications, however, samples are taken over finite scales larger than the Darcy scale (i.e. finite A) such that the actual pore-scale effect is suppressed and difficult to detect due to the mixing in the sampling volume. In addition, if sampling is over finite *time intervals* it can only enhance the mixing in sampling (e.g. Destouni & Graham 1997).

The first-order approximation for the velocity field, distributional assumptions for τ and η , and an assumption for relating Lagrangian and Eulerian statistics, have been employed in this analysis for illustrative purposes. Extensive numerical simulations (e.g. Bellin *et al.* 1992; Chin & Wang 1992; Cvetkovic *et al.* 1996) as well as comparison with field data (Burr, Sudicky & Naff 1994) support distributional assumptions and indicate that the first-order approximation is robust for σ_k^2 at least up to 1. In real applications and for higher σ_k^2 , numerical simulations can be used for determining distributions for τ and η as well as for computing their relevant statistics.

Knowledge of first two moments of the solute flux (or discharge) is often of direct practical interest, for instance, in risk management, remedial decisions, etc. However, the sampling practice in aquifers is most frequently in terms of flux-averaged concentration that is defined as $C_f = q/Vn$ [ML^{-3}] and hence directly related to the solute flux. The groundwater flux at a point of measurement is proportional to Vn and thereby also a random process; its statistics need to be combined with solute flux statistics to yield the flux-averaged concentration statistics. For example, $\langle C_f \rangle = (1/n) \int (q/V) f(q, V) dq dV$ defines the mean flux-averaged concentration (assuming constant effective porosity) where $f(q, V)$ denotes the joint p.d.f. between the solute flux and groundwater velocity for a specific sampling scale. Thus, the solute flux statistics provide a basis for evaluating the statistics of the flux-averaged concentration. The ability of the proposed framework to account for a finite sampling scale (i.e. $A > 0$) is crucial for conversion of the solute flux into the flux-averaged concentration data.

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Appendix

Let $f(X, Y; a)$ denote a joint p.d.f. of X and Y , which is dependent on a parameter a . Let $\hat{f}(p, q; a)$ denote the moment generating function of f that has been obtained as

an appropriate transform of f where p and q are transform variables. The moments of f are computed as

$$\mu_{mn} \equiv \int \int X^m Y^n f(X, Y; a) dX dY = (-1)^{m+n} \frac{\partial^{m+n} \hat{f}(p, q; a)}{\partial p^m \partial q^n} \quad (\text{A } 1)$$

for $p = q = 0$.

Let $F(X, Y)$ be defined as

$$F(X, Y) \equiv [f] = \frac{1}{A} \int_A f(X, Y; a) da, \quad (\text{A } 2)$$

where $a \in A$; thus F is also a p.d.f. We wish to compute the moments of F as functions of the moments of f .

Applying the linear integral operator $[\]$ on both sides of (A 1) yields

$$[\mu_{mn}] \equiv \int \int X^m Y^n F(X, Y) dX dY = (-1)^{m+n} \frac{\partial^{m+n} \hat{F}(p, q)}{\partial p^m \partial q^n} \quad (\text{A } 3)$$

since $\hat{F} = [\hat{f}]$. Thus, the moments of $F \equiv [f]$ are equal to the moments of f on which $[\]$ is applied. If the averaged joint moments are zero, we have $F(X, Y) = F(X)F(Y)$. The above can be generalized to three or more random variables.

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