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Transport of kinetically sorbing solute by steady random velocity in heterogeneous porous formations

By VLADIMIR CVETKOVIC[1] AND GEDEON DAGAN[2]

[1] Department of Water Resources Engineering, Royal Institute of Technology, S-10044 Stockholm, Sweden

[2] Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Israel

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A Lagrangian framework is used for analysing reactive solute transport by a steady random velocity field, which is associated with flow through a heterogeneous porous formation. The reaction considered is kinetically controlled sorption–desorption. Transport is quantified by the expected values of spatial and temporal moments that are derived as functions of the non-reactive moments and a distribution function which characterizes sorption kinetics. Thus the results of this study generalize the previously obtained results for transport of non-reactive solutes in heterogeneous formations (Dagan 1984; Dagan *et al.* 1992). The results are illustrated for first-order linear sorption reactions. The general effect of sorption is to retard the solute movement. For short time, the transport process coincides with a non-reactive case, whereas for large time sorption is in equilibrium and solute is simply retarded by a factor $R = 1+K_d$, where K_d is the partitioning coefficient. Within these limits, the interaction between the heterogeneity and kinetics yields characteristic nonlinearities in the first three spatial moments. Asymmetry in the spatial solute distribution is a typical kinetic effect. Critical parameters that control sorptive transport asymptotically are the ratio ϵ_r between a typical reaction length and the longitudinal effective (non-reactive) dispersivity, and K_d. The asymptotic effective dispersivity for equilibrium conditions is derived as a function of parameters ϵ_r and K_d. A qualitative agreement with field data is illustrated for the zero- and first-order spatial moments.

1. Introduction

Most subsurface formations exhibit significant and seemingly erratic spatial variability in their hydraulic properties. For a given constant average hydraulic gradient, heterogeneity of hydraulic properties of aquifers determines heterogeneity of the fluid seepage velocity by which dissolved contaminants are advected. In turn, variations in the fluid velocity control field-scale dispersion of non-reactive (conservative) solute that is frequently several orders of magnitude greater than the pore-scale dispersion and molecular diffusion (Dagan 1987, 1989).

Transport of non-reactive solute by random velocity fields in heterogeneous formations has been considered in several theoretical studies (e.g. Dagan 1982, 1984; Gelhar & Axness 1983; Neuman, Winter & Newman 1987; Neuman 1993; Shapiro & Cvetkovic 1988; Rubin 1990; Dagan, Cvetkovic & Shapiro 1992). In particular, the first and second moments of the solute spatial distribution were related to the statistics of the hydraulic conductivity under ergodic conditions for non-Fickian and Fickian regimes (Dagan 1982, 1984). Furthermore, the expected values of spatial moments of non-reactive solute plumes have been related to the solute source size for non-ergodic transport (Dagan 1984, 1990, 1991). Experimental data from two comprehensive field investigations conducted and reported in the literature to date (Borden site, Ontario, Canada, and Cape Cod site, Cape Cod, Mass. – Freyberg 1986; Hess, Wolf & Celia 1992), as well as results from numerial simulation (Bellin, Salandin & Rinaldo 1992; Chin & Wang 1992) compare favourably with the theoretical results of Dagan (1984).

Many subsurface contaminants of practical interest, however, are not conservative and undergo some type of reaction, the most common being sorption. Whereas random spatial variability in solute advection enhances contaminant spreading, sorption reactions tend to retard (or delay) solute movement; thus their role is often critical when assessing the potential impact of contaminants in the subsurface (Weber, McGinley & Katz 1991).

Sorption reactions are due to chemical and/or physical processes and imply an exchange of solute mass between the mobile fluid and immobile regions existing in the porous medium on different scales (Brusseau & Rao 1989; Weber *et al.* 1991; Sardin *et al.* 1991). In particular, solid grains constitute an immobile solid phase on the pore scale, onto which solute is (ad)sorbed by chemical reactions (e.g. ion-exchange). On the laboratory scale (10^{-1}–10^{0} M) and larger, regions of essentially stagnant fluid are found (e.g. intra-aggregate porosity, low-conductivity lenses); these regions constitute an immobile fluid phase. Owing to concentration gradients, solute mass is transferred between the mobile and immobile fluid phase by Fickian diffusion; this is referred to as physical sorption, or mass transfer.

The rate of mass transfer has a timescale whose ratio to a typical advection timescale constitutes an important parameter characterizing transport. A large mass transfer rate implies fast reactions that can be approximated as equilibrium. For low mass transfer rates, the reactions are rate-limiting (slow), and the kinetics of sorption is significant. The chemical sorption reactions can be either fast or rate-limiting, whereas physical mass transfer is generally rate-limiting.

It has been common in engineering applications to assume that sorption reactions are sufficiently fast such that equilibrium conditions prevail. Several recent theoretical studies have been focused on equilibrium sorption (Kabala & Sposito 1991; Chrysikopoulos, Kitanidis & Roberts 1992). Mounting evidence from both field and laboratory investigations indicates, however, that on the field-sale sorption rates are lower than generally assumed and that kinetic effects may be significant (Nkedi-Kizza *et al.* 1983; Miller & Weber 1986; Roberts, Goltz & Mackay 1986; Goltz & Roberts 1986; Ptacek & Gillham 1992). This is particularly true for transport in fractured formations (Knapp 1989).

Analytical solutions for transport that couple advection with kinetically controlled sorption in heterogeneous aquifers are limited in number. Deterministic solutions for either concentration or for the moments of the solute spatial distribution have been discussed for homogeneous porous media by van Genuchten & Wierenga (1976), Valocchi (1985) and Goltz & Roberts (1986, 1987). Transport of kinetically sorbing solute in aquifers of simple heterogeneity (stratifications) has also been addressed (Valocchi 1989; Andricevic & Foufoula-Georgiou 1991). The mass flux of sorptive solute in heterogeneous aquifers has been considered using a stochastic analytical model (Cvetkovic & Shapiro 1990), and also using a semianalytical approach (Selroos & Cvetkovic 1992).

In this paper, kinetically controlled sorption reactions are coupled with solute advection by a random steady velocity field. Large-scale transport is quantified by the expected values of spatial and temporal moments that are derived as functions of the non-reactive moments and a distribution function which characterizes sorption kinetics. This distribution function is obtained as a solution of one-dimensional mass balance equations for the mobile and immobile solute where the independent variables are time and the travel time of non-reactive solute along a streamline (streamtube). Results are illustrated for transport of solute subject to rate-limiting sorption in three-dimensional, heterogeneous and statistically isotropic aquifers. Asymptotic results are derived where the apparent dispersivity for sorptive solute is expressed as a function of the non-reactive dispersivity (Dagan 1984), and sorption rate coefficients. The results have recently been extended to heterogeneous formations of anisotropic structures (Dagan & Cvetkovic 1993).

2. Problem description

We consider fluid flow through heterogeneous porous formations with spatially variable hydraulic properties, such as hydraulic conductivity, $K(\boldsymbol{x})$, and porosity, $n(\boldsymbol{x})$, where $\boldsymbol{x}(x_1, x_1, x_3)$ is a Cartesian coordinate vector. The seemingly erratic variations of the hydraulic properties on the one hand, and the uncertainty stemming from scarcity of measurements on the other, are set in a rational framework by regarding the hydraulic properties as random space functions (RSF).

The fluid seepage velocity $\boldsymbol{V}(V_1, V_2, V_3)$ satisfies the continuity equation $\nabla \cdot (n\boldsymbol{V}) = 0$, and is related to K, n and to the hydraulic head Φ through Darcy's law $\boldsymbol{V} = -(K/n) \nabla\Phi$. Hence $\boldsymbol{V}$ is in turn an RSF which may also depend on time. We assume here that $\boldsymbol{V}$ is given in a statistical sense, and, below, we shall employ pertinent results derived in the past. To simplify matters, we limit the study to a time-independent and statistically stationary $\boldsymbol{V}$, and without loss of generality the mean flow is taken in the direction x_1.

Let a reactive solute of mass M_0 be injected into the flow field $\boldsymbol{V}(\boldsymbol{x})$ at time t_0 within a volume $\mathscr{V}_0$. The governing equations of solute mass balance on the Darcy scale have the form

$$n\frac{\partial C}{\partial t} + \nabla \cdot \boldsymbol{q} = -n\frac{\partial N}{\partial t}, \quad \text{i.e.} \quad \frac{\partial C}{\partial t} + \boldsymbol{V}\cdot\nabla C = -\frac{\partial N}{\partial t}, \tag{2.1a}$$

$$F(\partial N/\partial t, N, C) = 0, \tag{2.1b}$$

where C is the solute concentration in the fluid (mobile) phase, and N is the solute concentration (per unit fluid volume) that has been sorbed or transferred onto the solid (or immobile) phase, $\boldsymbol{q} = nC\boldsymbol{V}$ is the advective mass flux, and t is time. The function F in (2.1b) is a general expression for sorption kinetics that relates $\partial N/\partial t$ to C and N in a deterministic manner. The limiting case are equilibrium sorption reactions for which (2.1b) reduces to $F(C, N) = 0$.

Equations (2.1) couple two important processes of field-scale contaminant transport: (i) solute advection by the random velocity field, $C\boldsymbol{V}$, and (ii) resistances to solute advection due to rate-limiting (kinetic) mass transfer from the mobile to the immobile regions of the flow. In (2.1) only reversible sorption is accounted for; irreversible mass transfer (i.e. mass loss due to degradation, or decay) may be accounted for by adding a sink term in (2.1a). The mass transfer from the mobile to the immobile regions occurs because of chemical and/or physical processes. In most cases of practical interest, however, the rate-limiting mass transfer due to physical and chemical processes will be indistinguishable on the field scale (e.g. Brusseau & Rao 1989), and is therefore regarded as a single process. The direct effect of pore-scale dispersion and molecular diffusion, which was neglected in (2.1), is discussed in §7; the indirect effect of molecular diffusion through mass transfer is accounted for in the kinetics of (2.1).

Owing to the random nature of $V(\boldsymbol{x})$, solute concentrations, C and N in (2.1), are also random functions. The expected value of concentration, $\langle C\rangle$, can be represented in terms of the expected values of the moments of the solute spatial distribution that are related to the statistics of the Eulerian field $V(\boldsymbol{x})$. An alternative representation of transport is by means of the mass flux, $\boldsymbol{q}$. The expected mass flux over a control surface can be determined from expected temporal (travel time) moments that are related to the statistics of V. The representations of transport with the expected concentration and the expected mass flux can be related in special cases, such as for diffusion processes. In the general case, these two representations are independent and are both of interest for practical applications (Simmons 1982; Dagan *et al.* 1992).

In the following Sections, we adopt the Lagrangian approach to analyse the expected spatial and temporal moments of the mobile solute, as means of quantifying field-scale transport of kinetically sorbing solute.

3. Lagrangian formulation of transport

3.1. *Kinematical preliminaries*

The starting point of the Lagrangian approach is the Eulerian velocity field, $V(\boldsymbol{x})$, that is determined through Darcy's law from the pressure distribution. The vector equation of the fluid particle trajectory is $\boldsymbol{x} = \boldsymbol{X}(t; t_0, \boldsymbol{a})$, where $\boldsymbol{x} = \boldsymbol{a}$ is the initial coordinate at $t = t_0$, i.e. $\boldsymbol{X}(t_0; t_0, \boldsymbol{a}) = \boldsymbol{a}$. Steady flows are characterized by $\boldsymbol{X}(t; t_0, \boldsymbol{a}) = \boldsymbol{X}(t-t_0; \boldsymbol{a})$, where the $\boldsymbol{X}$ have to be determined from the differential system $\mathrm{d}\boldsymbol{X}/\mathrm{d}t = V(\boldsymbol{X})$, with $\boldsymbol{X}(t_0; \boldsymbol{a}) = \boldsymbol{a}$.

An alternative parametrization of the trajectories that is particularly useful in the present context is obtained first by inverting the relationship $x_1 = X_1(t-t_0; \boldsymbol{a})$ to yield $t-t_0 = \tau(x_1; \boldsymbol{a})$. It is seen that τ is the travel time of a fluid particle from the initial plane at $x_1 = a_1$ to the plane at x_1 (we shall denominate this plane as CP, the control plane, following the nomenclature of Dagan *et al.* 1992). We assume that the mean flow is in the x_1 direction and that τ is positive and finite, i.e. all fluid particles cross the CP at one time or another.

Substituting $t-t_0 = \tau(x_1; \boldsymbol{a})$ into the expressions for the transverse displacements X_2 and X_3, we obtain $\eta(x_1; a) = X_2(\tau; \boldsymbol{a})$ and $\zeta(x_1; \boldsymbol{a}) = X_3(\tau; \boldsymbol{a})$ (figure 1). Since $\mathrm{d}t = (\mathrm{d}\tau/\mathrm{d}x_1)\,\mathrm{d}x_1$, it follows that τ, η and ζ satisfy the differential system (Dagan *et al.* 1992)

$$\frac{\mathrm{d}\tau}{\mathrm{d}x_1} = \frac{1}{V_1(x_1, \eta, \zeta)}; \quad \frac{\mathrm{d}\eta}{\mathrm{d}x_1} = \frac{V_2(x_1, \eta, \zeta)}{V_1(x_1, \eta, \zeta)}; \quad \frac{\mathrm{d}\zeta}{\mathrm{d}x_1} = \frac{V_3(x_1, \eta, \zeta)}{V_1(x_1, \eta, \zeta)}, \tag{3.1}$$

with initial conditions $\tau = 0$, $\eta = a_2$ and $\zeta = a_3$ for $x_1 = a_1$. Hence, $x_2 = \eta(x_1; \boldsymbol{a})$ and $x_3 = \zeta(x_1; \boldsymbol{a})$ are simply the equations of the streamlines of the steady velocity field. The important feature of representation (3.1) is that the transverse coordinates η and ζ can be determined from the velocity field independent of τ. Furthermore, the inequality $X_1 > x_1$ implies a fluid particle that has moved beyond the CP, and is equivalent to $t-t_0 > \tau$. This can be expressed as $H(t-t_0-\tau) = 1-H(x_1-X_1)$, differentiation of which with respect to t yields

$$\delta(t-t_0-\tau) = V_1(x_1, \eta, \zeta)\,\delta(x_1-X_1) = V_1(\boldsymbol{X})\,\delta(x_1-X_1), \tag{3.2}$$

where H is the Heaviside step function, and δ is the Dirac delta function.

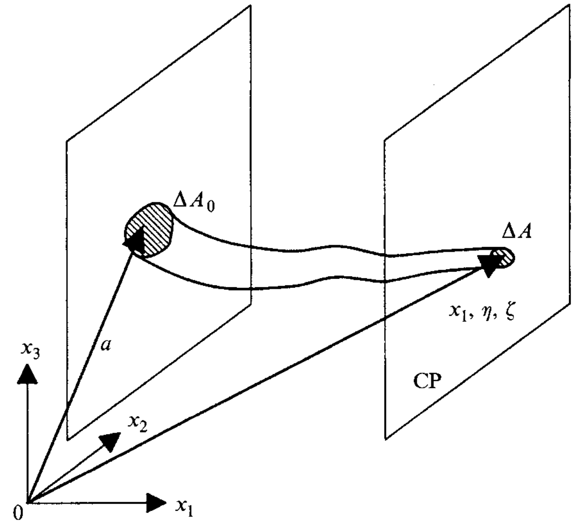

FIGURE 1. Definition sketch of a streamtube.

We consider now an infinitesimal streamtube (figure 1) originating from the plane $x_1 = a_1$ and of cross-sectional area $\Delta A_0 = \Delta a_2 \Delta a_3$. Assuming that the fluid moving through ΔA_0 during an infinitesimal time Δt_0 is tagged, the marked particle volume is given by $\Delta \mathcal{V}_0 = n_0 \Delta a_1 \Delta a_2 \Delta a_3$, where $\Delta a_1 = V_0 \Delta t_0$; for briefness, we have set $n_0 \equiv n(\boldsymbol{a})$ and $V_0 \equiv V_1(\boldsymbol{a})$. The Lagrangian statement of fluid continuity is as follows:

$$\Delta \mathcal{V}_0 = \Delta \mathcal{V}, \quad \text{i.e.} \quad n_0 \Delta a_1 \Delta a_2 \Delta a_3 = n \Delta X_1 \Delta X_2 \Delta X_3. \tag{3.3}$$

The usual Eulerian statement of continuity is $n_0 V_0 \Delta A_0 = n V_1(x_1, \eta, \zeta) \Delta A$, which is obtained by dividing (3.3) by $\Delta t = \Delta t_0$. The latter equality results from the differentiation of $t - t_0 = \tau(x_1; \boldsymbol{a})$ for fixed x_1 and $\boldsymbol{a}$. The fluid particle volume can therefore be expressed as follows:

$$\Delta \mathcal{V} = \Delta \mathcal{V}_0 = n_0 V_0 \Delta A_0 \Delta t_0 = n V_1(x_1, \eta, \zeta) \Delta A \Delta t. \tag{3.4}$$

The above convenient relationships will be used in the developments below.

3.2. *Concentration and mass flux*

3.2.1. *Non-reactive solute*

Let $C(\boldsymbol{x}, t)$ define the concentration (or the resident concentration in the terminology suggested by Kreft & Zuber 1978), as mass of solute per volume of fluid; the conservation of mass is expressed with the aid of (3.3) as

$$\Delta m = \Delta m_0, \quad \text{i.e.} \quad \Delta m_0 = n C(\boldsymbol{X}, t) \Delta \boldsymbol{X} = n_0 C_0(\boldsymbol{a}) \Delta \boldsymbol{a}, \tag{3.5}$$

where $\Delta \boldsymbol{a} \equiv \Delta a_1 \Delta a_2 \Delta a_3$, and similarly for $\Delta \boldsymbol{X}$. Let $\Delta C(\boldsymbol{x}, t)$ be equal to C for $\boldsymbol{x} \in \Delta \boldsymbol{X}$ and equal to zero outside $\Delta \boldsymbol{X}$. Then, for $\Delta \boldsymbol{X} \rightarrow 0$, (3.5) leads to

$$\Delta C = \frac{1}{n} \Delta m_0 \frac{1}{\Delta \boldsymbol{X}} \rightarrow \frac{1}{n} \Delta m_0 \, \delta(\boldsymbol{x} - \boldsymbol{X}) = \frac{1}{n} \Delta m_0 \frac{\delta(t - t_0 - \tau)}{V_1(x_1, \eta, \zeta)} \delta(x_2 - \eta) \, \delta(x_3 - \zeta), \tag{3.6}$$

where we have employed (3.2) and the definition of η, ζ preceding (3.1). Equation (3.6) in the form $\Delta C = (\Delta m_0 / n) \, \delta(\boldsymbol{x} - \boldsymbol{X})$ was the starting point of Dagan (1982, 1984) and will be used subsequently.

An alternative representation of transport is in terms of the solute flux

$$q(x_1, \eta, \zeta, t) = nV_1(x_1, \eta, \zeta)\, C(x_1, \eta, \zeta, t),$$

defined as mass of solute per unit area and unit time at a point on the CP. Defining again $\Delta q = q$ for points within $\Delta A = \Delta\eta\,\Delta\zeta$ in the CP and for $\tau < t - t_0 < \tau + \Delta t$, while $\Delta q = 0$ outside $\Delta A, \Delta t$, we may write, using (3.4) or (3.6),

$$\Delta q = \Delta m_0 \frac{1}{\Delta A\,\Delta t} \rightarrow \Delta m_0\, \delta(x_2 - \eta)\, \delta(x_3 - \zeta)\, \delta(t - t_0 - \tau). \tag{3.7}$$

The latter definition in (3.7) was the starting point of the analysis of transport in terms of the flux by Dagan *et al.* (1992) and Cvetkovic, Shapiro & Dagan (1992). Integration of Δq over η and ζ yields ΔQ, the solute flux through the entire CP, for an instantaneous injection of duration $\Delta t_0 \rightarrow 0$. This was used previously by Shapiro & Cvetkovic (1988). Furthermore, the total solute flux Q, divided by the total fluid flux, may be used for defining the flux-averaged concentration (Kreft & Zuber 1978). In the terminology of Kreft & Zuber (1978), the representation with the aid of the resident, or flux-averaged concentration at the CP, are detection modes. We may also use the resident concentration or solute flux representations at the inlet plane $x_1 = a_1$, referred to as injection modes (Kreft & Zuber 1978). This distinction is achieved by replacing in (3.6) or (3.7) Δm_0 by $n_0 C_0 \Delta a$ or by $q_0 \Delta A_0 \Delta t_0$, respectively. Here $C_0 = C(\boldsymbol{a}, t_0)$ is the initial concentration whereas $q_0 = q(\boldsymbol{a}, t_0)$ is the initial solute flux. If injection takes place at constant concentration, $q_0 = C_0 V_0$ is no longer constant since V_0 is spatially variable. This issue is discussed in our work in progress about continuously injected plumes.

3.2.2. *Reactive solute*

Here we wish to relate C in (2.1) to the Lagrangian variables X_i ($i = 1, 2, 3$), or τ, η, ζ that have been employed for representing transport of conservative solutes. At first glance this is not plausible, since following solute particles was equivalent to following fluid particles in motion, whereas in the present case part of the solute mass is immobilized. This apparent difficulty can be overcome by transferring (2.1) to a coordinate system (ξ_1, ξ_2, ξ_3) attached to streamlines and defined as follows:

$$\xi_1(\boldsymbol{x}; \boldsymbol{a}) = \tau(x_1; \boldsymbol{a}); \quad \xi_2(\boldsymbol{x}; \boldsymbol{a}) = x_2 - \eta(x_1; \boldsymbol{a}); \quad \xi_3(\boldsymbol{x}; \boldsymbol{a}) = x_3 - \zeta(x_1; \boldsymbol{a}). \tag{3.8}$$

The equation satisfied by $C(\xi, t)$ and $N(\xi, t)$ is obtained from (2.1) using (3.8) and (3.1) as

$$\frac{\partial C}{\partial t} + \nu \frac{\partial C}{\partial \xi_1} + [V_2(\boldsymbol{x}) - \nu V_2(x_1, \eta, \zeta)] \frac{\partial C}{\partial \xi_2} + [V_3(\boldsymbol{x}) - \nu V_3(x_1, \eta, \zeta)] \frac{\partial C}{\partial \xi_3} = -\frac{\partial N}{\partial t}, \tag{3.9}$$

where $\nu \equiv V_1(\boldsymbol{x}) / V_1(x_1, \eta, \zeta)$.

For $x_2 = \eta$ and $x_3 = \zeta$, i.e. along the streamline $\xi_2 = \xi_3 = 0$, (3.9) reduces to

$$\frac{\partial C}{\partial t} + \frac{\partial C}{\partial \xi_1} = -\frac{\partial N}{\partial t}, \tag{3.10}$$

where $C(\xi_1, 0, 0, t)$ and $N(\xi_1, 0, 0, t)$ are functions of two variables only. We solve (3.10) for instantaneous injection of solute in the mobile phase of concentration C_0 during a time interval Δt_0 at $x_1 = a_1$, i.e. at $\xi_1 = 0$. At the same injection site we assume that

$N(0,0,0,t)=0$, while the initial conditions are $C=0$, $N=0$ for $\xi_1>0$, $t=t_0$. With $\Delta t_0\to 0$, the boundary and initial conditions become

$$\Delta C(0,0,0,t)=C_0(\boldsymbol{a},t_0)\,\delta(t-t_0)\,\Delta t_0;\quad N(0,0,0,t)=0. \tag{3.11}$$

The solution of (3.10) with initial conditions (3.11) is the same as that of one-dimensional flow of unit velocity. Such a system has been the object of earlier studies and solutions are available for several types of sorption reactions. We shall write the solution in the general form

$$\Delta C(\xi_1,0,0,t)=C_0(\boldsymbol{a},t_0)\,\gamma(t-t_0,\tau)\,\Delta t_0, \tag{3.12}$$

thereby restricting our present discussion to processes where ΔC is linear in the initial concentration C_0. The form of the function γ depends on the particular process that was represented in a general form by (2.1 *b*). Thus, γ is derived explicitly in §5 for linear kinetics. If the reaction is nonlinear, γ may depend on C_0 and the initial concentration, and the manner in which the present analysis applies the results for a solute particle to a finite plume need to be modified. In the simplest case of a conservative solute, the solution of (3.10) with $N\equiv 0$ is $\gamma(t-t_0,\tau)=\delta(t-t_0-\tau)$, i.e. the solute particle crosses the CP at $t=t_0+\tau$, as does the fluid particle.

Because we are interested in finite initial input zones, we consider now an infinitesimal fluid streamtube entering ΔA_0 at $\boldsymbol{x}=\boldsymbol{a}$ (figure 1). We wish to express the concentration field ΔC, (3.12), in terms of the initial solute mass Δm_0 attached to a fluid particle of volume $\Delta\mathscr{V}_0$, (3.4), at $\boldsymbol{x}=\boldsymbol{a}$, $t=t_0$ while $\Delta C=0$ elsewhere. Since by (3.4) $\Delta m_0=C_0\,\Delta\mathscr{V}_0=n_0\,V_0\,\Delta A_0\,C_0\,\Delta t_0$, substitution in (3.12) yields

$$\Delta C(\xi_1,0,0,t)\equiv\Delta C(x_1,\eta,\zeta,t)=\frac{1}{n_0}\Delta m_0\,\gamma(t-t_0,\tau)\frac{1}{\Delta A_0\,V_0}, \tag{3.13a}$$

i.e.

$$\Delta C(x_1,\eta,\zeta,t)=\frac{1}{n}\Delta m_0\frac{\gamma(t-t_0,\tau)}{V_1(x_1,\eta,\zeta)}\frac{1}{\Delta A}. \tag{3.13b}$$

With $\Delta A\to 0$ and since $\Delta C=0$ outside the streamtube, one has

$$1/\Delta A\to\delta(x_2-\eta)\,\delta(x_3-\zeta).$$

Hence, ΔC can be written in the following final form:

$$\Delta C(x_1,\eta,\zeta,t;\boldsymbol{a})=\frac{1}{n}\Delta m_0\frac{\gamma(t-t_0,\tau)}{V_1(x_1,\eta,\zeta)}\delta(x_2-\eta)\,\delta(x_3-\zeta), \tag{3.14}$$

where the dependence on $\boldsymbol{a}$ in the right-hand side of (3.14) is due to that of τ,η,ζ on $\boldsymbol{a}$ as well of Δm_0.

The solute flux $\Delta q(\xi_1,0,0,t)=nV_1(x_1,\eta,\zeta)\,\Delta C$ is obtained from (3.14) as follows:

$$\Delta q(\boldsymbol{x},t-t_0;\boldsymbol{a})=\Delta m_0(\boldsymbol{a},t)\,\gamma(\tau,t-t_0)\,\delta(x_2-\eta)\,\delta(x_3-\zeta). \tag{3.15}$$

Equations (3.14) and (3.15) constitute the generalization of (3.6) and (3.7), respectively, to reactive solute. For conservative solute, $\gamma(\tau,t)=\delta(t-\tau)$ and with the aid of (3.2), (3.14) and (3.15) reduce to (3.6) and (3.7), respectively. Whereas for a conservative solute the mass is attached to the fluid particle, $\gamma(\tau,t)$ quantifies a trailing solute plume behind the fluid particle located at $\boldsymbol{x}=\boldsymbol{X}(t-t_0;\boldsymbol{a})$ or equivalently at

$\tau(x_1; \boldsymbol{a}) = t - t_0$, $x_2 = \eta(x_1; \boldsymbol{a})$, $x_3 = \zeta(x_1; \boldsymbol{a})$. Thus the reaction induces a distribution of the solute along the fluid streamline, but not across it. Matters are different if transverse diffusion is accounted for or if the fluid flow is unsteady. These cases are not considered at present.

Finally, the two injection modes can be expressed with the aid of (3.14) or (3.15) by substituting $\Delta m_0 = C_0(\boldsymbol{a})\,\mathrm{d}\boldsymbol{a}$ $(t_0 = 0)$, or $\Delta m_0 = q_0(\boldsymbol{a}, t_0)\,\Delta t_0$ for instantaneous resident concentration, or rate of inflow, respectively.

4. Expected spatial and temporal moments

We characterize a solute plume of finite volume by its spatial and temporal moments, which are random variables depending on t and x_1 respectively.

4.1. *Spatial moments*

The concentration field, C, for instantaneous injection of reactive solute into the finite volume $\mathscr{V}_0$ at $t_0 = 0$, is obtained by integrating ΔC (3.14) over $\mathscr{V}_0$. The result is

$$C(\boldsymbol{x}, t) = \frac{1}{n}\int_{\mathscr{V}_0} n_0\, C_0(\boldsymbol{a}) \frac{\gamma(t, \tau)}{V_1(x_1, \eta, \zeta)}\, \delta(x_2 - \eta)\, \delta(x_3 - \zeta)\, \mathrm{d}\boldsymbol{a}. \tag{4.1}$$

For non-reactive solute, $\gamma(\tau, t) = \delta(t - \tau)$, and (4.1) reduces by virtue of (3.2) to

$$C(\boldsymbol{x}, t) = \frac{1}{n}\int n_0\, C_0(\boldsymbol{a})\, \delta(\boldsymbol{x} - \boldsymbol{X})\, \mathrm{d}\boldsymbol{a}$$

which has been used in several previous studies (Dagan 1984, 1990) for investigating transport.

The spatial moments of the solute plume with respect to the origin are defined from (4.1) as

$$\mu_{mnr} = \int nCx_1^m\, x_2^n\, x_3^r\, \mathrm{d}\boldsymbol{x} = \int_{\mathscr{V}_0}\int_{a_1}^{\infty} n_0\, C_0(\boldsymbol{a})\, x_1^m\, \eta_2^n\, \zeta_3^r \frac{\gamma(t, \tau)}{V_1(x_1, \eta, \zeta)}\, \mathrm{d}x_1\, \mathrm{d}\boldsymbol{a} \tag{4.2}$$

since $\gamma(t, \tau) = 0$ for $x_1 < a_1$ (no backward reaction). The key to evaluating (4.2) is to exchange the variable x_1 with τ using (3.1) to obtain

$$\mu_{mnr} = \int_{\mathscr{V}_0}\int_0^{\infty} n_0\, C_0(\boldsymbol{a})\, [X_1(\tau; \boldsymbol{a})]^m\, [X_2(\tau; \boldsymbol{a})]^n\, [X_3(\tau; \boldsymbol{a})]^r\, \gamma(t, \tau)\, \mathrm{d}\tau\, \mathrm{d}\boldsymbol{a}, \tag{4.3}$$

where we account for the definition of τ, η, ζ preceding (3.1), i.e. $x_1 = X_1$, $\eta = X_2$ and $\zeta = X_3$.

Because the fluid velocity, $V(\boldsymbol{x})$, is assumed to be a stationary, random field, the kinematic variables $\boldsymbol{X}$, and thereby the spatial moments, μ_{mnr}, are random. For simplicity, we shall assume $C_0(\boldsymbol{a})$ to be deterministic, implying that the zero-order moment, μ_{000}, is deterministic. In the following, we wish to evaluate the statistical moments of the first three central spatial moments that are defined from μ_{mnr}. Although the following analysis may be used for evaluating statistical moments of different order, we restrict the present discussion to the expected values only. Furthermore, we shall assume that the ergodic hypothesis is obeyed for μ_{mnr}, a topic recently discussed for non-reactive solute by Dagan (1991). This requirement is ensured if $\mathscr{V}_0$ is of large extent compared to the velocity covariance integral scales.

Let Γ_p denote auxiliary functions defined as

$$\Gamma_p(t) \equiv \int_0^\infty \tau^p \gamma(t,\tau)\,\mathrm{d}\tau, \tag{4.4}$$

which depend on the particular type of reaction. The solute mass in the mobile phase, i.e. the zero-order moment, is obtained by setting $m = n = r = 0$ in (4.3) as

$$M(t) = M_0 \Gamma_0(t); \quad M_0 = \int_{\mathscr{V}_0} n_0 C_0(\boldsymbol{a})\,\mathrm{d}\boldsymbol{a}, \tag{4.5}$$

while the mass in the immobile phase is given by $M_0 - M(t)$. For a conservative solute, $\Gamma_p = t^p$, which is also the limit of Γ_p for $t \rightarrow 0$. Moreover, since Γ_p is positive, M decreases from M_0 at $t = 0$ to a smaller value, whereby the immobilized mass increases.

Next, the centroid coordinate $\boldsymbol{R}$ is obtained by taking one of the indices m, n or r equal to unity in (4.3), and normalizing by M (4.5) as follows:

$$\boldsymbol{R}(t) = \frac{1}{M}\int n\boldsymbol{x}C(\boldsymbol{x},t)\,\mathrm{d}\boldsymbol{x} = \frac{1}{M_0\Gamma_0}\int_{\mathscr{V}_0}\int_0^\infty n_0 C_0(\boldsymbol{a})\boldsymbol{X}(\tau;\boldsymbol{a})\gamma(t,\tau)\,\mathrm{d}\tau\,\mathrm{d}\boldsymbol{a}. \tag{4.6}$$

For a random velocity field of mean $\boldsymbol{U}(U,0,0)$ and for ergodic $\boldsymbol{R}$, we get for the ensemble mean

$$\langle R_1(t)\rangle = R_1(0) + U\Gamma_1/\Gamma_0; \quad \langle R_2\rangle = R_2(0), \quad \langle R_3\rangle = R_3(0), \tag{4.7}$$

where $R_1(0)$ is the deterministic initial centroid coordinate. Equation (4.7) is obtained using the result $\langle \boldsymbol{X}\rangle = \boldsymbol{a} + \boldsymbol{U}t$ (Dagan 1984) in (4.6).

The second central moment is defined as

$$\begin{aligned}\langle S_{ij}(t)\rangle &= \left\langle \frac{1}{M}\int nC(x_i - \langle R_i\rangle)(x_j - \langle R_j\rangle)\right\rangle \mathrm{d}\boldsymbol{x} \\ &= \frac{1}{M}\int_{\mathscr{V}_0}\int_0^\infty n_0\langle [X_i(\tau;\boldsymbol{a}) - \langle R_i(t)\rangle][X_j(\tau;\boldsymbol{a}) - \langle R_j(t)\rangle]\rangle C_0 \gamma(\tau,t)\,\mathrm{d}\tau\,\mathrm{d}\boldsymbol{a}.\end{aligned} \tag{4.8}$$

Substituting $\boldsymbol{X} = \boldsymbol{a} + \boldsymbol{U}t + \boldsymbol{X}'$, where $\boldsymbol{X}'$ is the fluctuation of $\boldsymbol{X}$, we get for the expected transverse moments, from (4.7), (4.4) and (4.3),

$$\langle S_{ij}(t)\rangle = S_{ij}(0) + \frac{1}{\Gamma_0}\int_0^\infty X_{ij}(\tau)\gamma(t,\tau)\,\mathrm{d}\tau \quad (i,j = 2,3), \tag{4.9}$$

and for the expected longitudinal moment

$$\langle S_{11}(t)\rangle = S_{11}(0) + U^2\frac{\Gamma_2}{\Gamma_0} - U^2\left(\frac{\Gamma_1}{\Gamma_0}\right)^2 + \frac{1}{\Gamma_0}\int_0^\infty X_{11}(\tau)\gamma(t,\tau)\,\mathrm{d}\tau, \tag{4.10}$$

where $X_{ij} \equiv \langle X_i' X_j'\rangle$ is the variance-covariance tensor of $\boldsymbol{X}$. Equation (4.10) encapsulates one of the main results of this study, expressing the reactive spatial variance as a function of the non-reactive spatial variance and the reaction-dependent coefficients Γ_p. Analytical expressions for X_{ij} as function of the hydraulic conductivity statistics have been obtained by Dagan (1982, 1984) assuming flow in unbounded domains; these expressions are to be defined and used in §6.

The first term of (4.10), $S_{11}(0) = (1/M_0)\int a_1^2 C_0\,\mathrm{d}\boldsymbol{a}$, is the initial second moment of the plume. The second and third terms in (4.10) exist for deterministic and uniform velocity fields and represent the spread of the solute due to mass transfer to the immobile phase. The last term in (4.10) is of major interest, since it couples the effects of velocity randomness and sorption. For a conservative solute, i.e. for $\gamma(t,\tau) = \delta(t-\tau)$ and $\Gamma_p = t^p$, (4.7)–(4.9) degenerate into familiar forms for non-reactive solute (Dagan 1984).

Finally, the longitudinal third central moment for reactive solute is given by

$$\begin{aligned}\langle S_{111}\rangle &= \frac{1}{M}\int_{\mathscr{V}_0}\int_0^{\infty} n_0\langle[X_1(\tau;\boldsymbol{a})-\langle R_1(t)\rangle]^3\rangle\, C_0\,\gamma(\tau,t)\,\mathrm{d}\tau\,\mathrm{d}\boldsymbol{a} \\ &= S_{111}(0)+U^3\frac{\Gamma_3}{\Gamma_0}+2U^3\left(\frac{\Gamma_1}{\Gamma_0}\right)^3-3U^3\frac{\Gamma_1\Gamma_2}{\Gamma_0^2}+\frac{3U}{\Gamma_0}\int_0^{\infty}\tau X_{11}\gamma\,\mathrm{d}\tau \\ &\quad -3U\frac{\Gamma_1}{\Gamma_0^2}\int_0^{\infty}X_{11}\gamma\,\mathrm{d}\tau, \end{aligned} \tag{4.11}$$

where we assume $\langle X_1'^3\rangle = 0$ (Dagan 1984).

4.2. *Temporal moments*

We compute here the temporal moments at a fixed control plane at x_1. Integrating first Δq, (3.15), over the CP, we obtain

$$\Delta Q(x_1, t-t_0;\boldsymbol{a}) = \Delta m_0\,\gamma(t-t_0,\tau). \tag{4.12}$$

Further integration of (4.12) over the injection volume $\mathscr{V}_0$ yields

$$Q(x_1, t-t_0) = \int_{\mathscr{V}_0} n_0\,C_0(\boldsymbol{a})\,\gamma[t-t_0,\tau(x_1;\boldsymbol{a})]\,\mathrm{d}\boldsymbol{a}, \tag{4.13}$$

which is to be used for evaluating the expected temporal moments. As a preparatory step we define the auxiliary coefficients

$$\Lambda_p(x_1) \equiv \int_0^{\infty} t^p\langle\gamma(t,\tau)\rangle\,\mathrm{d}t. \tag{4.14}$$

Because of the random character of $V(\boldsymbol{x})$, τ is a random variable following (3.1). Hence, the computation of $\langle\gamma\rangle$ in (4.14) requires knowledge of the probability density function of τ. For conservative solute, $\Lambda_p = \langle\tau^p\rangle$.

The expected cumulative breakthrough curve that is identical to the actual one under the ergodic conditions, is defined by

$$\langle M(x_1,t)\rangle/M_0 = \frac{1}{M_0}\int_0^t\langle Q(x_1,t'\rangle\,\mathrm{d}t' = \frac{1}{M_0}\int_0^t\int_{\mathscr{V}_0} n_0\,C_0(\boldsymbol{a})\,\langle\gamma(t',\tau)\rangle\,\mathrm{d}\boldsymbol{a}\,\mathrm{d}t', \tag{4.15}$$

with $\langle M(x_1,\infty)\rangle/M_0 = 1$ and for simplicity $\mathscr{V}_0$ is a disk at the plane $x_1 = a_1$.

The first three temporal moments can be evaluated from (4.13) using (4.14); we get for the mean passage time

$$\langle T(x_1)\rangle = \frac{1}{M_0}\int_0^{\infty} t'\langle Q(x_1,t')\rangle\,\mathrm{d}t' = \Lambda_1. \tag{4.16}$$

In a similar manner, we get for the second temporal moment

$$\langle S_T(x_1)\rangle = \frac{1}{M_0}\int_0^{\infty}(t'-\langle T\rangle)^2\langle Q(x_1,t')\rangle\,\mathrm{d}t' = \Lambda_2-\frac{2\Lambda_1^2}{\Lambda_0}+\frac{\Lambda_1^2}{\Lambda_0^2}. \tag{4.17}$$

For conservative solute $A_0 = 1$, $A_1 = \langle\tau\rangle$ and $A_2 = \sigma_\tau^2 + \langle\tau\rangle$, and (4.15)–(4.17) degenerate into expressions for conservative solute. Analytical expressions for $\langle\tau\rangle$ and σ_τ^2 as function of the hydraulic conductivity statistics, have been obtained by Shapiro & Cvetkovic (1988) under conditions identical to those considered by Dagan (1982, 1984). Equations (4.15), (4.16) and (4.17) generalize the results for conservative solutes to the case of reactive ones.

5. Linear sorption reactions

For evaluating the expected spatial and temporal moments as discussed in §4, the distribution function γ, (3.12), is required. In this section, we find γ for one important class of mass transfer (sorption) reactions, namely, for linear sorption, which has frequently been used for modelling reactive transport on both the field scale and in laboratory columns.

Let $\hat{C}$ and $\hat{N}$ denote the Laplace transforms of the mobile concentration, C, and the immobile concentration, N, respectively. The linear mass transfer models are defined such that the ratio $\hat{N}/\hat{C}$ is either a constant or a function of the Laplace transform variable, s (Villermaux 1974). Transforming the governing equation of mass balance (3.10) (with $\xi_1 = \tau$), we write for the linear sorption models

$$\frac{\mathrm{d}\hat{C}}{\mathrm{d}\tau} = -s(\hat{N}+\hat{C}); \quad \hat{N}/\hat{C} = W(s), \tag{5.1}$$

where $M(s)$ defines the mass transfer kinetics in the Laplace domain; the form of $W(s)$ depends on the type of mass transfer process assumed. For instantaneous injection (see (3.11)) of unit mass, the Laplace transform of γ (3.12), $\hat{\gamma}$, is obtained from (5.1) as

$$\hat{\gamma}(\tau, s) = \exp\{-s[1+W(s)]\,\tau\}. \tag{5.2}$$

Inversion of (5.2) for specific forms of $W(s)$ yields the γ that is to be used for evaluating the spatial and temporal moments.

A special case of interest is when the mass transfer between mobile and immobile zones is sufficiently fast relative to the timescale of the transport problem such that equilibrium may be assumed. For equilibrium conditions, $W(s) = \text{const} = K_d$, where K_d is referred to as the mass partitioning coefficient, or the equilibrium distribution coefficient (e.g. Valocchi 1985). Inverting (5.2), for the equilibrium case we obtain $\gamma(\tau, t) = \delta(t-\tau R)$, i.e. the advection of reactive solute is retarded relative to the advection of non-reactive solute by a factor $R = 1+K_d$; the parameter R is referred to as the retardation factor. In the absence of reactions, $W(s) = 0$, and $\gamma(t, \tau) = \delta(t-\tau)$.

5.1. *First-order rate model*

A number of different physical and chemical processes in porous media result in non-equilibrium mass transfer between mobile and immobile regions that can be described with the first-order rate model (Brusseau & Rao 1989; Weber *et al.* 1991; Sardin *et al.* 1991). The governing equations for advective transport coupled with the first-order rate of sorption are

$$\frac{\partial C}{\partial t}+\frac{\partial C}{\partial \tau} = -\frac{\partial N}{\partial t}-k_0\,C, \tag{5.3a}$$

$$\frac{\partial N}{\partial t} = k_1\,C-k_2\,N-k_0\,N \equiv k_2(K_d\,C-N)-k_0\,N, \tag{5.3b}$$

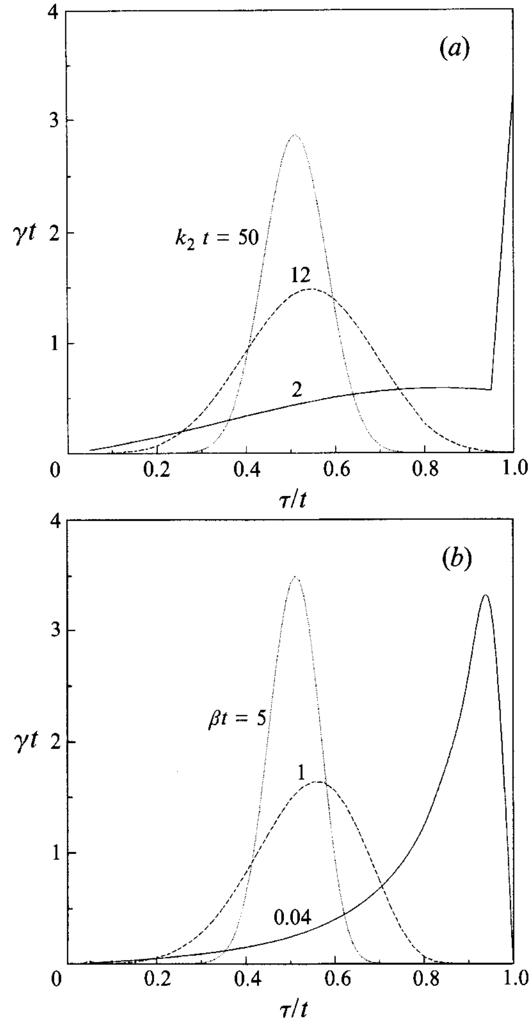

FIGURE 2. The distribution function γ at $K_d = 1$ for (*a*) first-order rate model (5.5), and (*b*) spherical diffusion model (5.8).

where k_1 and k_2 are the forward and backward rate coefficients, respectively, $K_d \equiv k_1/k_2$, and where we have included linear irreversible mass transfer (degradation, or decay), with k_0 being the decay rate. From the Laplace transform of (5.3*b*), $W(s)$ is obtained as

$$W(s) = \frac{K_d}{1+s/k_2+k_0/k_2}. \tag{5.4}$$

For sufficiently large k_2 (with K_d remaining constant), (5.4) reduces to the linear equilibrium model, i.e. $W(s) \rightarrow K_d$ for $k_2 \rightarrow \infty$ and $k_0 = 0$. By appropriate scaling of k_1 and k_2, simultaneous linear equilibrium sorption may be introduced in (5.3), whereby the so-called two-site model is obtained (e.g. Cameron & Klute 1977). Thus (5.3) represents a relatively general model for linear sorption reactions that can incorporate equilibrium and non-equilibrium linear reversible mass transfer, as well as the irreversible linear mass loss (decay).

The function γ is obtained for a pulse injection by inverting (5.2) with (5.4) (Lassey 1988):

$$\gamma(\tau, t) = \exp[-(k_1+k_0)\,t]\,\delta(t-\tau) \\ +k_1 k_2 \tau \exp(-k_1\tau - k_2 t + k_2\tau - k_0 t)\,\tilde{I}_1[k_1 k_2 \tau(t-\tau)]\,H(t-\tau), \quad (5.5)$$

where $\tilde{I}_1(Z) \equiv I_1(2Z^{\frac{1}{2}})/Z^{\frac{1}{2}}$ with I_1 being the modified Bessel function of the first kind of order one; the Laplace transform of γ is given by (5.2) with $W(s)$ defined in (5.4). Dimensionless γt obtained from (5.5) is illustrated in figure 2(*a*) as a function of τ/t for three values of $k_2 t$ for fixed K_d and for $k_0 = 0$. Note that figure 2(*a*) illustrates the approximate spatial distribution of solute along the streamtube; for a constant velocity field, the curves in figure 2(*a*) are proportional to the spatial distribution of solute. For large $k_2 t \rightarrow 0$ the reaction is not felt and $\gamma \rightarrow \delta(t-\tau)$.

5.2. *Diffusion models*

For applications where the physical mass transfer processes are dominant, and where the regions of the immobile fluid are not well mixed, the first-order rate model may not be sufficient for describing the mass transfer. For such cases, mass transfer models have been developed that assume a specific idealized geometry of the immobile regions (e.g. spherical, cylindrical, rectangular) within which the mass transfer is governed by Fick's second law of diffusion. The idealized geometry of the immobile regions may represent grains, soil aggregates, low-permeability zones, or blocks of rock. The diffusion models have been used for describing mass transfer in soils (van Genuchten & Wierenga 1977; van Genuchten & Dalton 1986), aquifers (Goltz & Roberts 1986) and fractured formations (Neretnieks & Rasmuson 1984).

The mass transfer equation (2.1*b*) for the diffusion models assuming three types of immobile geometry, are (Goltz & Roberts 1987)

$$\frac{\partial C^*}{\partial t} = \frac{D}{r^{m-1}}\frac{\partial}{\partial r}\left(r^{m-1}\frac{\partial C^*}{\partial r}\right); \quad N = \frac{m}{b^m}\int_0^b K_d\, r^{m-1} C^*\,\mathrm{d}r. \quad (5.6)$$

Equations (5.3) and (5.6) constitute a complete system of mass balance equations for the diffusion models. In (5.6), $m = 1$ for a rectangular, $m = 2$ for a cylindrical, and $m = 3$ for a spherical immobile region geometry, D is the diffusion coefficient of the sorbing solute in the immobile region, C^* is the concentration at locations within the immobile region, and K_d is the solute capacity ratio of the immobile to mobile zones. The equation for N in (5.6) defines the volume-averaged immobile solute concentration, N, in term of C^*, while b represents a characteristic length of the immobile zone (radius, in the case of spherical or cylindrical geometry, and half-width in the case of rectangular geometry). The initial/boundary conditions applicable within the immobile region are

$$C^*(r,0;\tau) = 0; \quad C^*(0,t;\tau) \neq \infty; \quad C^*(b,t;\tau) = C(\tau,t). \quad (5.7)$$

The system of equations (5.3), (5.6) with (5.7) has been solved by Rosen (1952) for the spherical model ($m = 3$) with continuous injection. Differentiating the result of Rosen (1952, equation (26)) with respect to time, the function γ is obtained as (with $k_0 = 0$)

$$\gamma(\tau, t) = \frac{4\beta}{\pi}\int_0^\infty \exp[-3K_d\beta\tau H_1(\lambda)]\cos[2\beta(t-\tau)\lambda^2 - 3K_d\beta\tau H_2(\lambda)]\,\lambda\,\mathrm{d}\lambda, \quad (5.8)$$

where $\beta \equiv D/b^2$ characterizes the kinetics of mass transfer and corresponds to k_2 in the first-order rate model; the functions H_1 and H_2 are defined as

$$H_1(\lambda) \equiv \frac{\lambda(\sinh 2\lambda + \sin 2\lambda)}{(\cosh 2\lambda - \cos 2\lambda)} - 1; \quad H_2(\lambda) \equiv \frac{\lambda(\sinh 2\lambda - \sin 2\lambda)}{(\cosh 2\lambda - \cos 2\lambda)}$$

and are well approximated by $H_1 = \lambda - 1$, and $H_2 = \lambda$ for $\lambda > 10$. Dimensionless γt obtained from (5.9) is illustrated in figure 2(*b*) as a function of τ/t for a few values of βt. With the appropriate choice of the parameters k_2, β and K_d, the first-order and the spherical diffusion models yield similar responses (figure 2).

The function $W(s)$ for the spherical diffusion model is (e.g. Goltz & Roberts 1987)

$$W(s) = \frac{3K_d\, i_1(\psi b)}{\psi b i_0(\psi b)}, \tag{5.9}$$

where i_n is the modified spherical Bessel function of the first kind of order n, i.e. $i_n(z) = (\pi/2z)^{\frac{1}{2}} I_{n+\frac{1}{2}}(z)$, with $I_{n+\frac{1}{2}}$ being the modified Bessel function of the first kind of order $n+\frac{1}{2}$, and where $\psi \equiv (s/D)^{\frac{1}{2}}$. The Laplace transform of γ (5.2) with $W(s)$ defined in (5.9).

The function $W(s)$ for the cylindrical geometry of the immobile regions is defined as $W(s) = 3K_d I_1(\beta b)/\beta b I_0(\beta b)$, whereas for the rectangular geometry it is

$$W(s) = K_d \tanh(\beta b)/\beta b$$

(Goltz & Roberts 1987). Following a similar methodology for Laplace inversion as that given by Rosen (1952), the γ-functions can be determined for the cylindrical and rectangular geometry.

The uniform and regular immobile-region geometry considered in the diffusion models is an overly simplified assumption for most field applications. However, these models capture the qualitative features of the rate-limiting, diffusion-controlled mass transfer, and as such have been used as an approximation even in formations where the geometry of the immobile regions is irregular and varying. For varying size of immobile zones, the characteristic length b is to be interpreted as an average, or effective value.

6. Illustration example

We consider solute transport in a three-dimensional, statistically isotropic heterogeneous porous medium under flow conditions identical to the ones discussed by Dagan (1984). In particular, the porosity of the medium, n, is assumed constant, whereby the fluctuations in the steady-state velocity field, V, are due solely to the spatial variability in the hydraulic conductivity, $K = K(x)$. The hydraulic conductivity is assumed to be lognormally distributed, i.e. $K(x) = K_G \exp(Y(x))$, where K_G is the geometric mean of K, and the distribution of Y is $N(0, \sigma_Y^2)$. The covariance function for Y is hypothesized as a negative exponential, i.e.

$$\langle Y(x)\, Y(x')\rangle = C_Y(|x-x'|) = C_Y(h) = \sigma_Y^2 \exp(-h/I),$$

where I is the integral scale of Y. Without loss of generality, we assume that the mean hydraulic gradient is parallel to the x_1-coordinate axis, i.e. $J(J,0,0)$; consequently, the mean flow is parallel to the x_1-coordinate axis, i.e. $U(U,0,0)$.

The controlling mechanism of the transport is assumed to be solute advection through the random flow field with simultaneous exchange of solute mass with the immobile regions of the medium. We assume rate-limiting mass transfer that is due to chemical and/or physical processes, and can be described by the linear first-order rate model (5.3).

In the following, we illustrate the effect of first-order linear sorption on solute transport. The effect of sorption kinetics on the expected first three moments of the spatial distribution (spatial moments) is illustrated in §6.1. The expected first three moments of reactive solute residence time (temporal moments) are illustrated in §6.2.

6.1. *Spatial moments*

The expected values of the first two spatial moments of a non-reacting solute advected in a three-dimensional, statistically isotropic heterogeneous porous medium are given by (Dagan 1982, 1984)

$$\langle X_1 \rangle = Ut = \frac{K_G J}{n} t; \quad \langle X_2 \rangle = \langle X_3 \rangle = 0 \tag{6.1}$$

and

$$\left.\begin{aligned} X_{11} &= 2U^2 I^2 \sigma_Y^2 \left[t' - \frac{8}{3} + \frac{4}{t'} - \frac{8}{t'^3} + 8\,\mathrm{e}^{-t'} \left(1 + \frac{1}{t'}\right) \frac{1}{t'^2} \right], \\ X_{22} = X_{33} &= 2U^2 I^2 \sigma_Y^2 \left[\frac{1}{3} - \frac{1}{t'} + \frac{4}{t'^3} - \mathrm{e}^{-t'} \left(\frac{1}{t'} + \frac{4}{t'^2} + \frac{4}{t'^3} \right) \right], \end{aligned}\right\} \tag{6.2}$$

where $\langle X_1 \rangle$ is the mean displacement in the x_1-direction, and X_{ij} are the variances in the three directions, with $X_{ij} = 0$ for $i \neq j$. The dimensionless time is defined as $t' \equiv t/t_h$, where $t_h \equiv I/U$ is a characteristic time of the formation heterogeneity. Equations (6.1) and (6.2) are first-order approximations in σ_Y^2, implying that X is Gaussian and all the moments can be expressed with the aid of $\langle X_1 \rangle$ and X_{ij} (Dagan 1984).

In order to evaluate spatial moments for reactive solute, the Γ-functions (4.4) need to be determined. For $\gamma(\tau, t)$ defined in (5.5), the first four Γ-functions are, for $k_0 = 0$ (Appendix A),

$$\Gamma_0 = \frac{1}{R}(1 + K_d \,\mathrm{e}^{-t''}) \tag{6.3a}$$

$$\Gamma_1 = \frac{1}{R^2}(1 + K_d^2 \,\mathrm{e}^{-t''})\, t'' + \frac{2K_d}{R^2}(1 - \mathrm{e}^{-t''}), \tag{6.3b}$$

$$\Gamma_2 = \frac{6K_d(K_d - 1)}{R^3}(1 - \mathrm{e}^{-t''}) + \frac{K_d}{R^3}(1 - K_d \,\mathrm{e}^{-t''})\, t'' + \frac{1}{R^3}(1 + K_d^3 \,\mathrm{e}^{-t''})\, t''^2, \tag{6.3c}$$

$$\begin{aligned} \Gamma_3 = {} & \frac{12K_d(K_d - 1)}{R^3}(1 + \mathrm{e}^{-t''}) + \frac{1}{R^3}[6(K_d - 1)^2 - 12K_d](1 - K_d \,\mathrm{e}^{-t''}) \\ & - \frac{1}{R^4}(K_d - 1)[6K_d - (K_d - 1)^2](1 + K_d \,\mathrm{e}^{-t''}) \\ & + \frac{t''}{R^4}[24K_d(K_d - 1)(1 - \mathrm{e}^{-t''}) + 12K_d^2(1 + \mathrm{e}^{-t''})] \\ & + \frac{12K_d}{R^4}(1 - K_d^2 \,\mathrm{e}^{-t''})\, t''^2 + \frac{1}{R^4}(1 + K_d^4 \,\mathrm{e}^{-t''})\, t''^3, \end{aligned} \tag{6.3d}$$

where $t'' \equiv t/t_r$ is a dimensionless time and $t_r \equiv (k_2 R)^{-1}$ is a charcteristic reaction time.

Inserting (6.1)–(6.3) into (4.7)–(4.11), spatial moments for reactive solute are

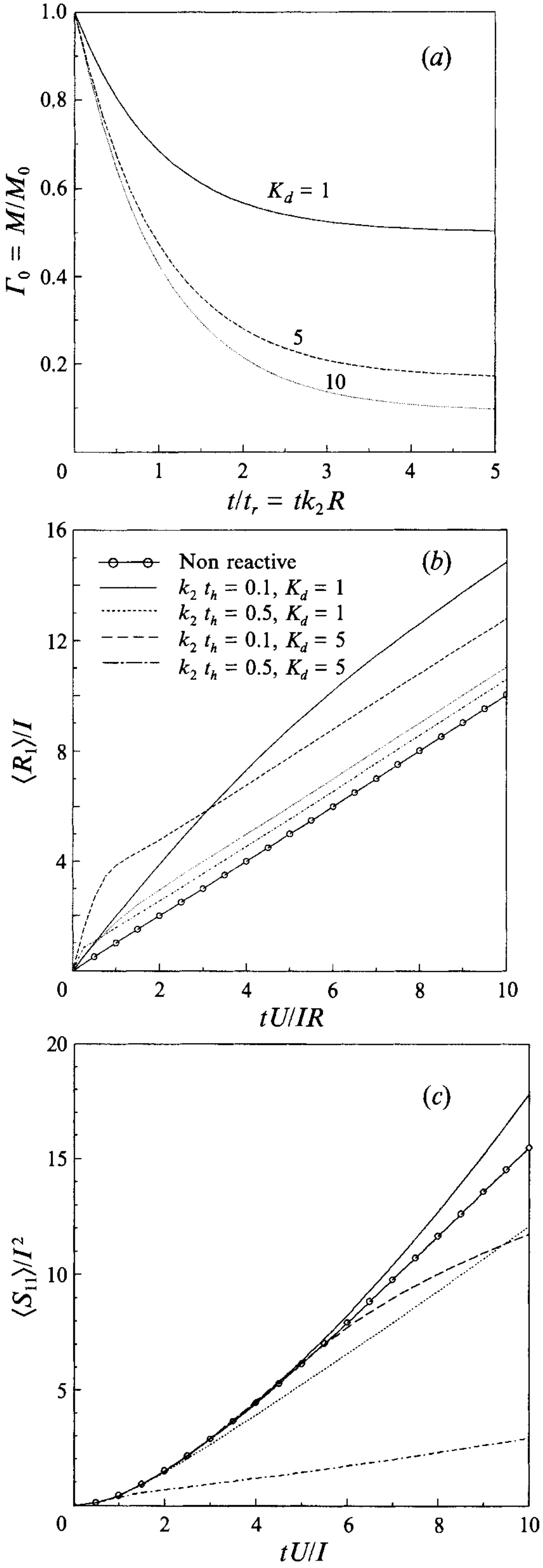

FIGURE 3(a–c). For caption see facing page.

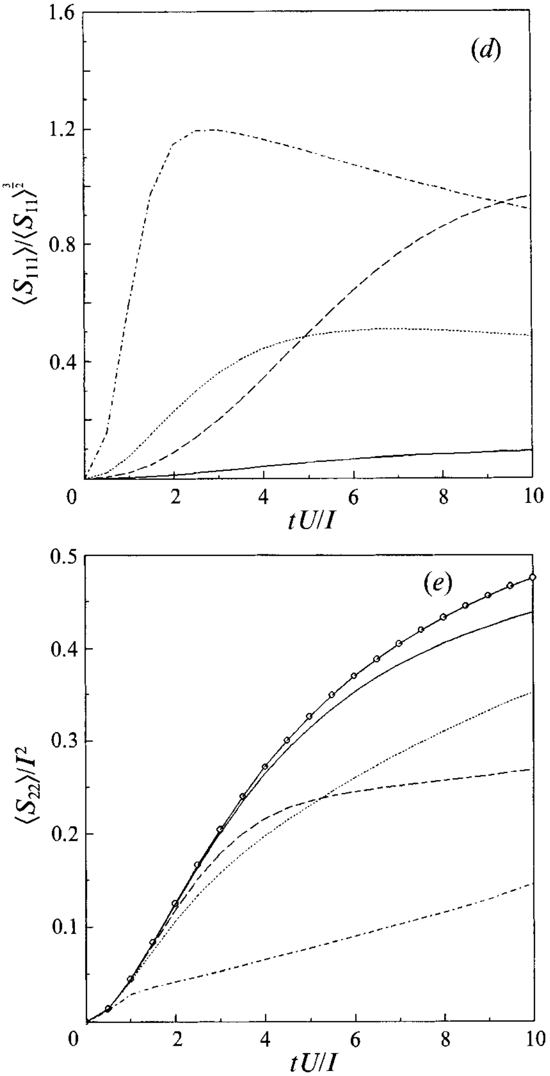

FIGURE 3. Expected values of central spatial moments evaluated from (4.5)–(4.11) for different $k_2 t_h$ and $K_d = k_1/k_2$ for $\sigma_Y^2 = 1$: (*a*) zero-order moment, (*b*) first-order moment, (*c*) second-order longitudinal moment, (*d*) coefficient of skewness, and (*e*) second-order transverse moment.

evaluated and illustrated in figure 3 over the range $0 < t/t_h < 10$ for different values of a dimensionless sorption parameter $k_2 t_h$ and of K_d. The ratio between the characteristic times of the reaction and of heterogeneity is $t_r/t_h = U(k_2 IR)^{-1}$, which for the selected values of $k_2 t_h$ and K_d in figure 3 is in the range $0.25 < t_r/t_h < 5$, i.e. $t_r/t_h = O(1)$. Thus, the moments illustrated in figure 3 may be considered in the non-Fickian, non-equilibrium (kinetic) regime.

The zero-order moment that quantifies immobilized mass is illustrated in figure 3 (*a*). The retardation of the reactive solute plume centroid compared to the non-reactive one is illustrated by the first spatial moment in figure 3(*b*). For small t/t_h, the effect of retardation is small, i.e. all curves branch from the one for conservative solute. At large t/t_h, the effect is retardation at a constant rate R (asymptotic cases are to be discussed subsequently). A similar effect is manifested for $\langle S_{ij}\rangle$, (4.9)–(4.10), i.e. branching out from the curve for conservative solute at small t/t_h, and the general decrease of the spreading rate in comparison to the conservative case at large t/t_h (figures 3*c*, *e*).

The nonlinearity in $\langle R_1\rangle$ is a typical kinetic effect (figure 3*b*) that is more pronounced for decreasing sorption rates, $k_2\,t_h$, and increasing partition coefficient, K_d. The nonlinearity in $\langle S_{11}\rangle$ (figure 3*c*) and in $\langle S_{22}\rangle = \langle S_{33}\rangle$ (figure 3*e*) is due to coupled non-Fickian and kinetic effects. The non-zero skewness is an indicator of non-equilibrium (kinetic) effects since $\langle X_1'^3\rangle = 0$ (figure 3*d*). Although for the illustrated curves skewness is positive, for decreasing $k_2\,t_h$ nd K_d, skewness attains negative values (see figure 4*b*).

Asymptotic results

The expressions for the spatial and temporal moments depend on three parameters of significance: a timescale characterizing heterogeneity, $t_h = I/U$, a reaction timescale, $t_r = (k_2 R)^{-1}$, and the partition coefficient, K_d (or $R = 1+K_d$). Various asymptotic limits of interest may be obtained depending on the ratio t_r/t_h, and on the timescale of the transport problem, t/t_h, or t/t_r, where t is the time elapsed from the onset of transport of a solute body injected instantaneously at $t = t_0 = 0$. Herein we discuss two such limits:

(i) *Non-equilibrium, Fickian regime.* We consider first the case where the timescale of the problem is much larger than the heterogeneity timescale, i.e. $t/t_h \gg 1$, whereas $t/t_r = O(1)$, implying $t_r/t_h \gg 1$. These conditions indicate Fickian transport for non-reactive solute (Dagan 1984), with kinetically controlled reactions. The appropriate expressions of the spatial moments are obtained from (6.2) as

$$X_{11} \rightarrow 2I^2\sigma_Y^2\,t'; \quad X_{22} = X_{33} \rightarrow \tfrac{2}{3}I^2\sigma_Y^2 \quad \text{for} \quad t' = t/t_h \rightarrow \infty. \tag{6.4}$$

Substitution of (6.4) into (4.5) and (4.7)–(4.11) yields

$$M/M_0 = \Gamma_0; \quad \langle R_1\rangle = U\Gamma_1/\Gamma_0; \tag{6.5a, b}$$

$$\langle S_{11}\rangle \rightarrow U^2\left(\frac{\Gamma_2}{\Gamma_0}-\frac{\Gamma_1^2}{\Gamma_0^2}\right)+2\sigma_Y^2\,I\langle R_1\rangle; \quad \langle S_{ij}\rangle \rightarrow \tfrac{2}{3}I^2\sigma_Y^2 \quad (i,j = 2,3); \tag{6.5c, d}$$

$$\langle S_{111}\rangle = U^3\left(\frac{\Gamma_3}{\Gamma_0}+2\frac{\Gamma_1^2}{\Gamma_0^3}-3\frac{\Gamma_1\Gamma_2}{\Gamma_0^2}\right)+6\sigma_Y^2\,IU^2\left(\frac{\Gamma_2}{\Gamma_0}-\frac{\Gamma_1^2}{\Gamma_0^2}\right), \tag{6.5e}$$

where for simplicity we have set $R_i(0) = S_{ij}(0) = 0$ $(i,j = 1,2,3)$.

The first term on the right-hand side of $\langle S_{11}\rangle$ in (6.5) is due to reaction kinetics, whereas the second term is related to heterogeneity, and is identical to the one prevailing for conservative solute with the mean displacement defined by $\langle R_1\rangle$ in (6.5), rather than being Ut. Furthermore, by the scaling $\langle S_{11}\rangle/U^2t_r^2$, this dimensionless function is a sum of two terms: the first-one depends on K_d and t/t_r, while the second is a function of t/t_r and K_d multiplied by $1/\epsilon_r$, where $\epsilon_r \equiv Ut_r/\sigma_Y^2 I = t_r/\sigma_Y^2\,t_h$; ϵ_r is a relevant dimensionless number quantifying the ratio between a reaction typical length Ut_r, and the longitudinal effective dispersivity for a conservative solute, $\alpha_L = \sigma_Y^2\,I$, evaluated from $\alpha_L = (1/2U)(\mathrm{d}X_{11}/\mathrm{d}t)$. For kinetically controlled transport, $1/\epsilon_r \ll 1$, and the first term is dominant. $\langle S_{11}\rangle/U^2t_r^2$ obtained from (6.5) is illustrated in figure 4(*a*) for different values of ϵ_r and K_d. A decomposition similar to that for $\langle S_{11}\rangle/U^2t_r^2$ is valid for $\langle S_{111}\rangle/U^3t_r^3$; skewness defined as $\langle S_{111}\rangle/\langle S_{11}\rangle^{\frac{3}{2}}$ is illustrated in figure 4(*b*) as a function of t/t_r for a few values of K_d and ϵ_r. The change of sign in skewness for increasing ϵ_r is due to the gradual shift of solute mass into the tail part of γ (figure 2*a*).

(ii) *Equilibrium regime.* If the timescale of the transport problem is much larger

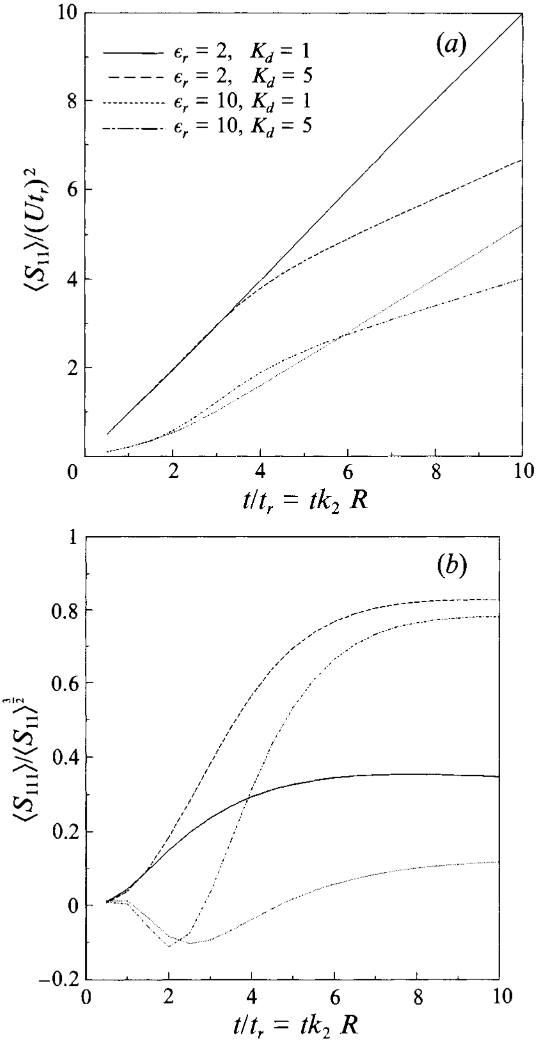

FIGURE 4. Expected values of asymptotic spatial moments (6.5) with $\sigma_Y^2 = 1$: (*a*) second-order longitudinal moment, and (*b*) coefficient of skewness.

than the reaction timescale, i.e. $t'' = t/t_r \gg 1$, equilibrium will prevail. With neglect of terms $O(e^{-t''})$ in (6.3) we get

$$\Gamma_0 \to \frac{1}{R}; \quad \frac{\Gamma_1}{t_r} \to \frac{2K_d}{R^2} + \frac{t''}{R^2}; \quad \frac{\Gamma_2}{t_r^2} \to \frac{K_d}{R^3} t'' + \frac{t''^2}{R^3} + \text{const}; \tag{6.6a–c}$$

$$\frac{\Gamma_3}{t_r^3} \to \frac{12K_d(K_d-2)}{R^4} t'' + \frac{12K_d}{R^4} t''^2 + \frac{t''^3}{R^4} + \text{const}. \tag{6.6d}$$

Substituting (6.6) into (4.5) and (4.7)–(4.10) yields

$$M/M_0 \to \frac{1}{R}; \quad \langle R_1 \rangle \to \frac{U}{R}\left(t + \frac{2K_d}{k_2 R}\right), \quad \text{i.e.} \quad \frac{\mathrm{d}\langle R_1 \rangle}{\mathrm{d}t} \to \frac{U}{R} \tag{6.7a–c}$$

$$\langle S_{11} \rangle \to \frac{2K_d U^2}{k_2 R^3} t + X_{11}(t/r); \quad \langle S_{ij} \rangle \to X_{ij}(t/R) \quad (i,j = 2,3); \tag{6.7d, e}$$

and where the skewness coefficient $\langle S_{111} \rangle / \langle S_{11} \rangle^{\frac{3}{2}}$ converges to zero as $t^{-\frac{1}{2}}$.

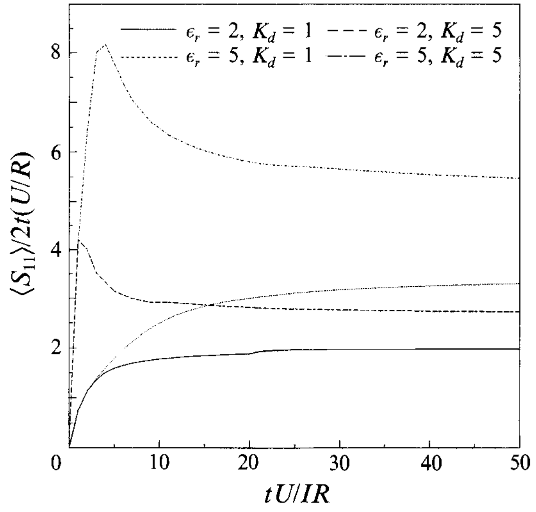

FIGURE 5. Expected value of effective (apparent) dispersivity evaluated using $\langle S_{11}\rangle$ in (4.10), for different $\epsilon_r = Ut_r/\sigma_Y^2 I = U/Rk_2\sigma_Y^2 I$ and $K_d = k_1/k_2$, and with $\sigma_Y^2 = 1$.

The equilibrium relationships (6.7) specify that $K_d M_0$ of the initial mass is sorbed, and that the solute-body centroid is retarded by $1/R$ relative to the fluid. Similarly, the heterogeneity-induced second spatial moment in (6.7) is obtained from that of a conservative solute by replacing t with the retarded time t/R.

It is appropriate to adopt in this case the dimensionless variable $t^* \equiv t/t_h R = tU/RI$ as the independent one. We may rewrite (6.7) in a dimensionless form as

$$\frac{\mathrm{d}(\langle R_1\rangle/IR)}{\mathrm{d}t^*} = 1; \quad \frac{\langle S_{11}\rangle}{\sigma_Y^2 I^2} = \frac{2K_d}{R}\epsilon_r t^* + X'_{11}(t^*), \tag{6.8a, b}$$

$$\frac{\langle S_{ij}\rangle}{\sigma_Y^2 I^2} = X'_{ij}(t^*) \quad (i,j = 2, 3), \tag{6.8c}$$

where $X'_{ij} \equiv X_{ij}/\sigma_Y^2 I^2$ and $\epsilon_r = Ut_r/\sigma_Y^2 I$. For transport dominated by heterogeneity, $\epsilon_r \ll 1$. This point becomes clearer if we consider in (6.8) the Fickian limit, i.e. $t^* = tU/RI \rightarrow \infty$. Substitution of (6.4) into (6.8) yields

$$\frac{\langle S_{11}\rangle}{\sigma_Y^2 I^2} = \frac{2K_d}{R}\epsilon_r t^* + 2t^*. \tag{6.9}$$

An apparent (effective) longitudinal dispersivity may be defined as

$$\alpha_L^* = \langle S_{11}\rangle R/2tU$$

(Dagan 1984). We then have from (6.9)

$$\frac{\alpha_L^*}{\sigma_Y^2 I} = \frac{K_d}{R}\epsilon_r + 1. \tag{6.10}$$

This simple expression relates the asymptotic effective dispersivity for conservative solute, $\alpha_L = \sigma_Y^2 I$, to the one prevailing in reactive solute transport under equilibrium conditions, the effects being additive.

The apparent dispersivity $\langle S_{11}\rangle R/2tU$ (with $\langle S_{11}\rangle$ defined in (4.10)) is illustrated in figure 5 as a function of tU/IR for different values of ϵ_r and K_d. For $K_d = 1$, the apparent dispersivity increases monotonically to its asymptotic value given by (6.10), similarly as for the non-reactive case (Dagan 1984). In comparison, for larger partitioning coefficient ($K_d = 5$), the apparent dispersivity attains a peak value during early time and then decreases to its asymptotic value given by (6.10).

6.2. *Temporal moments*

Assuming a travel time p.d.f. g_1 based on non-reactive temporal moments, the expected reactive solute flux at fixed locations was analysed by Cvetkovic & Shapiro (1990). Reactive temporal moments were analysed based on Monte Carlo simulation of two-dimensional porous media and using γ (5.5) in Selroos & Cvetkovic (1992). The focus here is on the analytical expressions for reactive temporal moments in the Fickian limit.

The non-reactive first two temporal moments for large $x' = x_1/I$ are defined as (Shapiro & Cvetkovic 1988; Dagan *et al.* 1992)

$$\langle \tau \rangle = x_1 n / K_G J = x_1/U; \quad \sigma_\tau^2 = 2\sigma_Y^2 I x_1/U^2 \quad \text{for} \quad x' = x_1/I \to \infty. \tag{6.11}$$

The first three temporal moments for sorptive solute can be evaluated provided that a particular form of g_1 is hypothesized using (6.11). For the purpose of this discussion, we assume an inverse-Gaussian p.d.f. g_1 (Shapiro & Cvetkovic 1988) the Laplace transform of which is

$$\hat{g}_1(s) = \exp\left[A' x_1 - x_1 (A'^2 + sA'')^{\frac{1}{2}}\right], \tag{6.12}$$

where $A' \equiv x_1/(\langle \tau \rangle U^3 \sigma_\tau^2)$ and $A'' = 2x_1/(U^3\sigma_\tau^2)$, with $\langle \tau \rangle$ and σ_τ^2 defined in (6.11). The inverse-Gaussian distribution for travel time is consistent with a diffusion process (Simmons 1982). The expected values of the first three central temporal moments for reactive solute $\langle T \rangle$, σ_T^2 and ν_T respectively, are evaluated using (5.5), (6.12), and (B 1) and (B 2) of Appendix B, as

$$\frac{\langle T \rangle}{IR/U} = x'; \quad \frac{\sigma_T^2}{2\sigma_Y^2 I^2 (R/U)^2} = \left(1 + \epsilon_r \frac{K_d}{R}\right) x', \tag{6.13a, b}$$

$$\frac{\nu_T}{12\sigma_Y^4 I^3 (R/U)^3} = \left(1 + \epsilon_r \frac{K_d}{R} + \epsilon_r^2 \frac{K_d}{4R}\right) x'. \tag{6.13c}$$

The first three temporal moments (6.13) are all linear functions of the distance, in contrast to the first three spatial moments, which are nonlinear functions of time (figures 3*b* and 4). Large ϵ_r implies strong kinetic effects that result in large asymmetry in the solute breakthrough which is quantified by ν_T (6.13*c*). This indicates the so-called 'tailing' phenomenon that is a typical kinetic effect where small amounts of solute are discharged into the advecting fluid (mobile region) from the immobile regions over prolonged periods of time; such effects have frequently been observed in both laboratory and field experiments (Weber *et al.* 1991).

6.3. *Comparison with field data*

Experimental data on field-scale transport of sorptive solute that is sufficiently detailed for moment analysis, is limited. At the Borden field site, Ontario, Canada, five halogenated hydrocarbons were injected as reactive (sorptive) tracers into the aquifer (with $U = 0.09$ m day^{-1}), and their movement was monitored for a period of two years. Only the zero-order and the first moments of the Borden field experiment are available in the literature. Data for the zero-order moment and the first moment for two hydrocarbons (bromoform (BROM) and *1,2*-dichlorobenzene (DCB)) are illustrated in figure 6, taken from Roberts *et al.* (1986). Figure 6 depicts the decrease of mobile solute mass with time due to immobilization, and is consistent with the type of curve given in figure 3(*a*). The nonlinear increase with time of the plume centroid position for the two hydrocarbons (figure 6*b*) resembles the curves of figure 3(*b*). The similarity between curves in figures 6(*a*) and 3(*a*), and figures 6(*b*) and 3(*b*) indicates that the

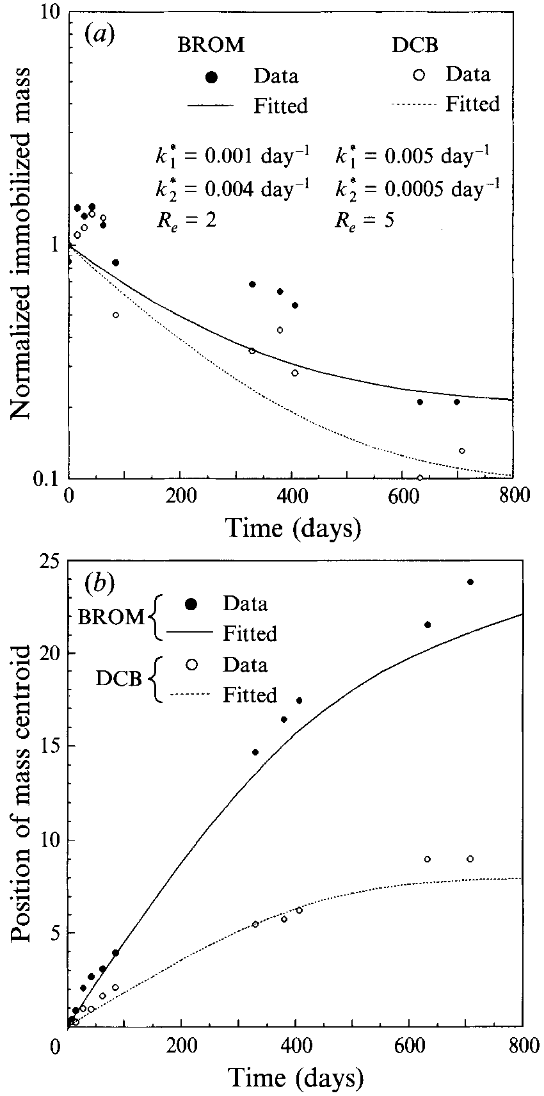

FIGURE 6. Field data from BROM and DCB from the Borden field experiment (from Roberts *et al.* 1986), and comparison with fitted curves obtained using the model of §5.1 modified into the two-site sorption model with $U = 0.09$ m day^{-1}: (*a*) zero-order moment, and (*b*) first-order moment.

prevailing sorption processes for BROM and DCB monitored in the Borden aquifer are qualitatively consistent with the first-order rate sorption model (5.3).

Recently, Ptacek & Gillham (1992) reported data on sorption parameters from small-scale experiments on samples from the Borden aquifer. Their analysis showed that the so-called two-site linear sorption model (e.g. Cameron & Klute 1977) most closely reproduces the sorption processes for the five hydrocarbons injected in the Borden aquifer. The two-site sorption of hydrophobic organic compounds such as BROM and DCB, is viewed as being controlled by an initial rapid reaction at the sorbent surface followed by diffusion into organic matter to additional sorption sites. The total reaction is thus a result of simultaneous equilibrium (fast) sorption quantified by a retardation factor R_e, and non-equilibrium (slow, diffusion-controlled) sorption characterized by rate coefficients, k_1^* and k_2^*.

The linear sorption model of §5.1 is readily extended to a two-site model by redefining the coefficients in (5.3) as $k_1 = k_1^*/R_e$ and $k_2 = k_2^*$ (Lassey 1988; Destouni & Cvetkovic 1991) and by evaluating τ from $\mathrm{d}\tau/\mathrm{d}x_1 = R_e\, V_1(x_1, \eta, \zeta)$ rather than from (3.1). The parameters k_1^*, k_2^* and R_e were chosen (with $k_0 = 0$ since no evidence of degradation has been reported) such as to provide a reasonable fit with the measured data (figure 6): $k_1^* = 0.001\ \mathrm{day}^{-1}$ and $k_2^* = 0.004\ \mathrm{day}^{-1}$ and $R_e = 2$ for BROM, and $k_1^* = 0.005\ \mathrm{day}^{-1}$ and $k_2^* = 0.0005\ \mathrm{day}^{-1}$ and $R_e = 5$ for DCB. In view of the relatively large 95% confidence interval for the zero-order-moment data, particularly at early time (Ptacek & Gillham 1992) the curves in figure 6 closely resemble the measured data. More data than those available from the Borden experiment is required, however, for a proper verification of the linear sorption model (5.3). It may be noted that the sorption parameters estimated in figure 6 differ significantly from those estimated in small-scale experiments by Ptacek & Gillham (1992). The small-scale data are consistent with the field-scale data only during the first month (Ptacek & Gillham 1992), whereas the field-scale data in figure 6 are for the entire monitoring period of two years.

7. Discussion of results and conclusions

Transport of a passive scalar by steady random velocity in a heterogeneous formation has been previously analysed using the Lagrangian framework (e.g. Dagan 1984, 1991). For a statistically stationary velocity field of uniform mean and under ergodic conditions, the solute-body centroid moves at the constant speed U, whereas its second-order spatial moments increase with time. Neglecting the effect of pore-scale dispersion, the growth of the transverse moments is limited and results from the winding of the streamlines in space. The longitudinal moment grows indefinitely due to the variation of the velocity among streamtubes. With $t_h = I/U$ being the heterogeneity characteristic time, and for $t/t_h \gg 1$, where t is the transport time, the longitudinal second moment grows linearly in time. In the asymptotic stage, the longitudinal effective dispersion coefficient is constant and the effective dispersivity, α_L, obtained by division by U, is at first order equal to $\sigma_Y^2 I$.

Similar results were obtained from the analysis of solute flux through a fixed control plane at say x_1 (Shapiro & Cvetkovic 1988; Dagan *et al.* 1992). The breakthrough curve is characterized by an average passage (travel) time $\langle\tau\rangle = x_1/U$. The temporal variance grows linearly with x_1 for $x_1/I \gg 1$ and is given at first-order by $\sigma_\tau^2 = 2I\sigma_Y^2 x_1/U^2$.

The main objective of the present study is to generalize these results to transport of a reactive solute that is sorbed reversibly by an immobile phase (soil aggregates, stagnant zones, rock matrix) while being advected by the fluid (mobile phase).

In principle, the Lagrangian framework is not suitable for the analysis of transport of sorptive solute since sorption immobilizes part of the solute particle mass and thus particles do not move as indivisible entities. By an appropriate nonlinear transformation, however, the transport equation is reduced to that of one-dimensional flow of unit velocity along streamlines (equation (3.10)). For such a case, a number of solutions are available in the literature that can readily be incorporated into the Lagrangian framework. The effect of sorption upon solute concentration in the mobile phase is manifested in the existence of a wake of solute trailing behind the solute particle. This wake, represented qualitatively in figure 2, is confined to the streamtubes of the fluid flow, no mechanism of transverse exchange being present.

The presence of pore-scale dispersion may have a significant effect upon the local concentration $C(x, t)$. Indeed, the convective mechanism results in the separation of the solute plume into parcels that move quicker than the mean through zones of higher permeability, with the opposite occurring in low-conductivity regions. In the absence of diffusion mechanisms and for a conservative solute, the concentration stays equal to its initial value. Since the lengthscale of solute parcels is the heterogeneity scale I, the pore-scale dispersion becomes effective in reducing local concentrations at $t \sim I^2/D_d$. However, this effect is negligible upon the longitudinal spatial or temporal moments of the entire plume, which are dominated by the spread of the parcels in space (for a discussion see Dagan 1989, Section 4.6). Pore-scale dispersion may affect more significantly the transverse spatial moments of the plume, since the convective mechanism leads to modest lateral growth (the plume tends to a constant second moment in three-dimensional flow and grows logarithmically with time in two-dimensional flow). Hence, for $t \sim l_T^2/D_{dT}$, where l_T is the initial lateral dimension of the plume and D_{dT} is the coefficient of transverse pore-scale dispersion, the plume lateral moments are affected by pore-scale dispersion. Owing to the smallness of D_{dT}, and to the ergodic plumes considered in the present study (large l_T/I), the above timescale is very large, beyond the range of interest in most applications.

The general results are illustrated for the case of linear kinetics with constant rate coefficients k_1 and k_2. The process is characterized by the reaction time $t_r = (k_2 R)^{-1}$ and the distribution coefficient $K_d = k_1/k_2$. While closed-form solutions are presented for spatial and temporal moments, the nature of the transport process is apparent in the asymptotic limits. For $t/t_h \ll 1$, the solute behaves like a passive tracer, as demonstrated by expansions in (6.3).

An interesting limit is $t/t_r \gg 1$ for which equilibrium is reached between phases in a batch experiment. In the spatial analysis, there is a partition of constant ratio K_d between the sorbed solute mass and the mass in the fluid (equation (6.7)). In contrast, the entire mass passes eventually through any control plane in the solute flux analysis. Under ergodic conditions, the solute-body centroid moves with constant retarded speed U/R, (6.7), and, similarly, the mean passage time is delayed by $R = 1+K_d$ ((6.13), valid for any x_1). The spatial transverse moments are identical to those pertinent to a conservative solute, apart from the retardation which differs by a factor R (6.7). The longitudinal second spatial moment, (6.7), consists of two terms. The first one is entirely related to sorption and prevails for uniform flow; it encapsulates the effect of the reactive trailing wake that is absent in the case of passive tracers. The second term is identical to the advective term retarded by R, (6.7). Hence for a fixed time, the first term augments dispersion whereas second one diminishes it.

The simplest asymptotic results are achieved for both $t/t_h \gg 1$ and $t/t_r \gg 1$, while the important dimensionless number $\epsilon_r = Ut_r/\sigma_Y^2 I$ represents the relative impact of sorption and spatial heterogeneity. Under these limits, the longitudinal effective dispersivity obtained from the division of the dispersion coefficient by the *retarded velocity*, consists of the aforementioned two terms: the advective one is the same as for a passive scalar, whereas the sorptive one is proportional to ϵ_r, (6.10). Thus a snapshot of the solute body at a fixed transport distance shows increased longitudinal spread for a reactive solute. Similar additive effects of sorption and heterogeneity are displayed by the temporal moments, (6.13).

At intermediate transport times or distances to the control plane, the process evolves from the first to the last limit in a complex manner as illustrated in figures 3 and 4. Although comprehensive data from field tests for moment analysis of reactive solute have yet to be collected, qualitative agreement has been found for the zero- and first-order spatial moments of the Border field experiment.

The analysis has focused on transport in porous heterogeneous formations. Its general part, however, is applicable to other similar processes with advection by steady random velocity fields. Several problems remain to be investigated in the future. For instance, the expressions for the spatial and temporal moments for non-ergodic conditions, similar to those discussed for non-reactive solute (Dagan 1991), are of particular interest. Furthermore, the extension of results to consider nonlinear sorption reactions, and other types of chemical reactions in porous media, is to be considered in the future.

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Appendix A

The Γ-functions (4.4) for first-order linear sorption may be evaluated as

$$\Gamma_p(t) \equiv \int_0^\infty \tau^p \gamma(t,\tau)\,\mathrm{d}\tau = (-1)^p \frac{\mathrm{d}^p\hat{\gamma}}{\mathrm{d}s^p}\bigg|_{s=0}, \tag{A 1}$$

where $\hat{\gamma}$ is the Laplace transform of γ over τ defined as

$$\hat{\gamma}(s,t) = \int_0^\infty \mathrm{e}^{-s\tau}\gamma(\tau,t)\,\mathrm{d}\tau \tag{A 2}$$

with γ given in (5.5). Noting that γ (5.5) is the solution of (5.3) for instantaneous injection of unit mass (i.e. for $\gamma(0,t) = C(0,t)/C_0\,\Delta t_0 = \delta(t)$), we apply the Laplace transform operator over τ on (5.3) (with $k_0 = 0$) to obtain the following system of differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{Bmatrix}\hat{\gamma}\\ \hat{\theta}\end{Bmatrix} = \begin{pmatrix}-(s+k_1+k_0) & k_2\\ k_1 & -k_2\end{pmatrix}\begin{Bmatrix}\hat{\gamma}\\ \hat{\theta}\end{Bmatrix}, \tag{A 3}$$

subject to $\hat{\gamma}(s,0) = 1$ and $\hat{\theta}(s,0) = 0$, where $\theta = N/C_0\,\Delta t_0$. The solution of (A 3) for $\hat{\gamma}$ is

$$\hat{\gamma}(s,t) = E_1 \exp(-\alpha_1 t) - E_2 \exp(-\alpha_2 t), \tag{A 4}$$

where
$$E_1 = (k_2+\alpha_1)/(\alpha_1-\alpha_2), \quad E_2 = (k_2+\alpha_2)/(\alpha_1-\alpha_2)$$
$$\alpha_{1,2} = -\tfrac{1}{2}(s+k_2R+k_0) \mp \tfrac{1}{2}((s+k_0)+2k_2(s+k_0)(K_d-1)+k_2^2R^2)^{\frac{1}{2}}$$

with $R = 1+K_d$ and $K_d = k_1/k_2$. Inserting (A 4) into (A 1), $\Gamma_p(p = 0,1,2,3)$ are evaluated as (6.3) after setting $k_0 = 0$ and normalizing with $t_r = (k_2R)^{-1}$.

Appendix B

The pth-order Λ-function (4.14) is evaluated as

$$\Lambda_p(x_1) \equiv \int_0^\infty t^p\langle\gamma\rangle\,\mathrm{d}t = (-1)^p\frac{\mathrm{d}^p}{\mathrm{d}s^p}\mathscr{L}[(\langle\gamma\rangle)]\,|_{s=0}, \tag{B 1}$$

where $\mathscr{L}(\langle\gamma\rangle) \equiv \int \mathrm{e}^{-st}\langle\gamma\rangle\,\mathrm{d}t$ is the Laplace transform of $\langle\gamma\rangle$. Furthermore, we may write

$$\mathscr{L}(\langle\gamma\rangle) \equiv \langle\hat{\gamma}\rangle = \int_0^\infty \hat{\gamma}(s,\tau)\,g_1(\tau)\,\mathrm{d}\tau. \tag{B 2}$$

The Laplace transform of g_1 is $\hat{g}_1(s) = \int \mathrm{e}^{-s\tau}g_1\,\mathrm{d}\tau$; substituting $\hat{\gamma}$, (5.4), into (B 2) we see that

$$\mathscr{L}(\langle\gamma\rangle) = \hat{g}_1(s') = \hat{g}_1\{s[1+W(s)]\}, \tag{B 3}$$

i.e. $s' = s[1+W(s)]$. Equation (B 3) implies that if the non-reactive travel time p.d.f., g_1, is known, and a particular $W(s)$ is assumed, then the reactive temporal moments may be evaluated using (B 1) and (B 3) without explicit knowledge of γ. A result analogous to (B 3) has been obtained by Villermaux (1974) for steady-state flow in a set of parallel tubes of constant radius; equation (B 3) is a generalization of this result to arbitrary steady-state flow fields.

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