Stochastic differential equations in the theory of solute transport through inhomogeneous porous media

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Abstract

Stochastic differential equations for solute transport are constructed from corresponding deterministic transport equations by re-interpreting their physical parameters as random functions of space and time. A partial differential equation for the ensemble-average solute concentration then can be derived from the stochastic transport equation by a cumulant expansion method used in non-equilibrium statistical mechanics. Examples of this approach are given for both conservative and reactive solutes moving through inhomogeneous porous media. The resulting ensemble-average transport equations are shown to be similar formally to their local-scale, deterministic analogs; but they exhibit additional, field-scale physical parameters arising from correlations among fluctuating, local-scale convective or reactive properties of the solute. Some unresolved conceptual issues attending the interpretation of the ensemble-average solute concentration and the field-scale parameters are discussed briefly.

1. Introduction

A significant body of research has begun to emerge in which the hypothesis is made that the transport properties of a porous medium in nature can be modeled as random functions parameterized by space and time coordinates [for reviews see Dagan (1986, 1987) and Sposito et al. (1986)]. The motivation for this approach is the observed, large variability of fundamental quantities, like the hydraulic conductivity (Sudicky, 1986) or the dissolved solute velocity (Biggar and Nielsen, 1976), at the field scale in natural porous media. This variability is pictured to have a random character, such that the transport properties of a single field-scale unit are represented as "sample-realizations" of random functions, or stochastic processes (Karlin and Taylor, 1975).

In their classical, non-stochastic setting, the transport properties of porous media are important because they figure directly in the partial differential equations which describe the time evolution of concentration variables for matter that moves by various mechanisms through these media. For example, the transport of a reactive dissolved solute with concentration, $c(\boldsymbol{x}, t)$, might be described with the equation (cf. van Genuchten and Alves, 1982):

$$\frac{\partial c}{\partial t} = (R^{-1}\nabla \cdot \overline{\overline{D}} \cdot \nabla - R^{-1}\boldsymbol{v} \cdot \nabla - b)\, c(\boldsymbol{x},t) \tag{1.1}$$

where $\overline{\overline{D}}$ is a dispersion tensor, R is a "retardation factor" for a linearly-adsorbing solute, $\boldsymbol{v}$ is a (uniform, constant) solute velocity, and b is a "decay constant" for a first-order loss rate (e.g., biodegradation) of the solute. If now the transport properties $\overline{\overline{D}}$, $\boldsymbol{v}$, R^{-1}, and b were to be interpreted as random functions because of their spatial variability, they would be replaced in (1.1) by sample realizations. A useful notation is, e.g., $\boldsymbol{V}(\boldsymbol{x}, t; \omega)$ to denote a stochastic solute velocity that depends on space and time coordinates, with the argument ω distinguishing it from a non-random velocity. Particular values of ω indicate particular samples, or realizations, of $\boldsymbol{V}(\boldsymbol{x}, t; \omega)$: $\boldsymbol{V}(\boldsymbol{x}, t; \omega_1)$, $\boldsymbol{V}(\boldsymbol{x}, t; \omega_2)$, etc. Thus (1.1) could be rewritten in a stochastic context:

$$\frac{\partial c}{\partial t} = [R^{-1}(\boldsymbol{x};\omega)\nabla \cdot \overline{\overline{D}} \cdot \nabla - R^{-1}(\boldsymbol{x};\omega)\, \boldsymbol{V}(\boldsymbol{x},t;\omega) \cdot \nabla - b(\boldsymbol{x};\omega)]\, c(\boldsymbol{x},t;\omega) \tag{1.2}$$

where $\overline{\overline{D}}$ has been left, as is customary, as a non-random coefficient because of its significantly smaller observed spatial variability as compared to the solute velocity (Dagan, 1984, 1987). The solution of (1.2) is a random function (a stochastic solute concentration) because the coefficients in (1.2) are random functions.

Equation (1.2) is an example of a stochastic partial differential equation. The general recipe for constructing such equations follows the procedure used to arrive at (1.2): the corresponding non-stochastic transport equation is written down, then one or more of its coefficients are modeled as random functions. Because of this representation of the coefficients as continuous random functions, there is an infinite number of possible solutions that satisfy the stochastic partial differential equation under given boundary and initial conditions. Evidently the statistical properties of the random coefficients must be prescribed in order to find ways to solve the resulting stochastic differential equation in a well-defined way. The ensemble-mean solution and its relationship to the low-order statistical properties of the coefficients are of particular relevance, as will be discussed below.

In this chapter, an introduction to the application of stochastic differential equations like (1.2) to the theory of solute transport will be presented. Emphasis will be placed on physical significance more than mathematical manipulation, with the hope that the relevance of the stochastic approach to transport in heterogeneous porous media can be appreciated. The basic mathematical techniques are outlined in Section 2, followed by physical examples in Sections 3 and 4. Section 5 closes the chapter with a discussion of two important (and unresolved) conceptual issues arising from the interpretation of stochastic differential equations in an average sense.

2. The cumulant expansion

2.1. Physical motivation

As stated above, a stochastic differential equation could be solved for all possible realizations of its coefficients to yield all possible realizations of its solution. In practice, this arduous task is seldom attempted and one looks instead for a way to calculate the ensemble average of the solution. This average is simply the product of the solution, indexed by ω, with the probability density function for ω, integrated over all ω. Conceptually, each realization of the solution of a stochastic differential equation corresponds to a specific example of the physical process governed by the equation (e.g., solute transport). This specific example, indexed by a value of ω, is assumed to occur in a finite fraction of a hypothetical infinitude of identical copies of the system to which the stochastic differential equation applies. The fraction associated with a given ω is equatable to its probability density function in the ensemble, and the product of this fraction and the corresponding realization of the solution, summed over all values of ω, is the ensemble-average solution. If the probability density function is not too broad, it will be sensible to interpret the ensemble-average solution as that to be observed in a single measurement.

A variety of mathematical techniques to derive ensemble-average solutions of stochastic differential equations has been described [see, e.g., reviews by van Kampen (1976), Winter et al. (1984), and Dagan (1987)]. One of the more physically transparent methods is the cumulant expansion (van Kampen, 1976, 1981, chapter 14). The essence of this approach is the assumption that a random coefficient in a stochastic differential equation has fluctuations in time whose root-mean-square amplitude, α, and autocorrelation time, τ_c, combine to make the product $\alpha\tau_c$ small. When this condition is met, a partial differential equation for the ensemble-average solution of a stochastic differential equation can be derived that is exact to order $(\alpha\tau_c)^2$ (van Kampen, 1976). This partial differential equation is similar in form to the original stochastic differential equation, but it exhibits coefficients that are modified by the random fluctuations inherent in the stochastic equation. So long as $\alpha\tau_c$ is small, this will be the only effect of the fluctuations on the ensemble-average equation.

2.2. Outline of the expansion

Consider the stochastic differential equation:

$$\frac{\partial y}{\partial t} = [A_0 + A_1(t)]\ y(\boldsymbol{x}, t; \omega) \qquad (t > 0) \tag{2.1}$$

where $y(\boldsymbol{x}, t; \omega)$ is a realization of the solution [like the solute concentration, $c(\boldsymbol{x}, t; \omega)$], A_0 is a non-random ("sure") operator, and $A_1(t)$ is a random operator acting on $y(\boldsymbol{x}, t; \omega)$. For example, if (2.1) were a solute transport equation and the only mechanism of transport were convection via the stochastic velocity $\boldsymbol{V}(\boldsymbol{x}, t; \omega)$, then, $A_0 = -\boldsymbol{v} \cdot \nabla$ and $A_1(t) = -\tilde{\boldsymbol{v}}(\boldsymbol{x}, t; \omega) \cdot \nabla$, where $\boldsymbol{v}$ is the ensemble-average of $\boldsymbol{V}(\boldsymbol{x}, t; \omega)$, assumed uniform and constant, and:

$$\tilde{\boldsymbol{v}}(\boldsymbol{x},t;\omega) \equiv \boldsymbol{V}(\boldsymbol{x},t;\omega) - \boldsymbol{v} \tag{2.2}$$

is the fluctuation about the average. If $A_1 \equiv 0$, the formal solution of (2.1) would be:

$$\begin{aligned} y(\boldsymbol{x},t) &= \exp(A_0 t)\, y(\boldsymbol{x},0) \\ &= \left[1 + A_0 t + \tfrac{1}{2} A_0^2 t^2 + \cdots\right] y(\boldsymbol{x},0) \end{aligned} \tag{2.3}$$

where "powers" of A_0 mean repeated applications of the operator. Equation (2.3) shows how the solution $y(\boldsymbol{x}, t)$ is propagated in time from the initial condition, $y(\boldsymbol{x}, 0)$.

The sure operator $\exp(A_0 t)$ is termed the "propagator" in this context. It can be used to eliminate the non-random part of (2.1) by the transformation:

$$y(\boldsymbol{x},t;\omega) \equiv \exp(A_0 t)\, u(\boldsymbol{x},t;\omega) \tag{2.4}$$

On differentiating both sides of (2.4) with respect to time and substituting the result into (2.1), one finds the stochastic differential equation:

$$\frac{\partial u}{\partial t} = \hat{A}_1(t)\, u(\boldsymbol{x},t;\omega) \qquad (t > 0) \tag{2.5}$$

where:

$$\hat{A}_1(t) \equiv \exp(-A_0 t)\, A_1(t)\, \exp(A_0 t) \tag{2.6}$$

The problem of solving (2.1) thus has been reduced to that of solving (2.5). The initial condition for the latter is arbitrary, but usually it is taken to be the sure function $y(\boldsymbol{x}, 0)$ as appears in (2.3). The randomness in $y(\boldsymbol{x}, t; \omega)$ then comes entirely from that of $\hat{A}_1(t)$ in (2.5). [Random initial conditions are straightforward to consider if they are statistically independent of $y(\boldsymbol{x}, t; \omega)$.] In the cumulant expansion approach, one notes that a formal solution of (2.5) like that in (2.3) is possible, and one then develops an expansion of the ensemble average of:

$$\exp\left[\int_0^t \hat{A}_1(t')\, \mathrm{d}t'\right]$$

to derive the approximate partial differential equation (van Kampen, 1976):

$$\frac{\partial \langle u \rangle}{\partial t} = \int_0^t \langle \hat{A}_1(t) \hat{A}_1(t') \rangle \mathrm{d}t' \langle u(\boldsymbol{x},t) \rangle \tag{2.7}$$

where $\langle\ \rangle$ represents an ensemble average. The corresponding approximate equation for $\langle y(\boldsymbol{x}, t)\rangle$ is (van Kampen, 1976):

$$\frac{\partial\langle y\rangle}{\partial t} = \left[A_0 + \int_0^t \langle\hat{A}_1(t)\hat{A}_1(t')\rangle \mathrm{d}t'\right]\langle y(\boldsymbol{x},t)\rangle \tag{2.8}$$

under the assumption that $\langle A_1(t)\rangle \equiv 0$.

Equation (2.8) is the partial differential equation of principal interest. It shows that the time evolution of $\langle y(\boldsymbol{x}, t)\rangle$ is governed by a sure operator, A_0, plus the time integral of the covariance function, $\langle\hat{A}_1(t)\hat{A}_1(t)\rangle$. This latter quantity is of order of $\alpha^2\tau_c$, where α^2 measures the magnitude of the covariance function and τ_c is the time scale over which it decays to zero. Hence $\langle y(\boldsymbol{x}, t)\rangle$ is estimated to order $(\alpha\tau_c)^2$. The fluctuations in $\hat{A}_1(t)$ lead, in this order of approximation, to a coefficient in the partial differential equation for $\langle y(\boldsymbol{x}, t)\rangle$ in addition to those contributed by the sure operator, A_0, in the corresponding non-random differential equation. This coefficient will be time-dependent so long as $t < \tau_c$, when the time-covariance function gives a non-negligible contribution to the integral in (2.8). After the time correlations decay, the integral term is effectively a constant like the sure operator.

3. Tracer solutes

3.1. *The stochastic velocity field*

In order to apply (2.8) to the movement of a tracer solute (i.e., a solute for which the only transport mechanisms are convection and dispersion), it is necessary to prescribe the statistical properties of the stochastic velocity field, $\boldsymbol{V}(\boldsymbol{x}, t; \omega)$. It is sufficient for illustrative purposes to assume that $\boldsymbol{V}(\boldsymbol{x}, t; \omega)$ is a divergence-free, wide-sense stationary, random function of position and time (Doob, 1953):

$$\nabla\cdot\boldsymbol{V} \equiv 0 \tag{3.1}$$

$$\langle\boldsymbol{V}(\boldsymbol{x},t)\rangle = \boldsymbol{v} \qquad \langle\bar{v}_i(\boldsymbol{x},t)\,\bar{v}_j(\boldsymbol{x}',t')\rangle = \Gamma_{ij}(\boldsymbol{x}-\boldsymbol{x}',t-t') \tag{3.2}$$

where $\boldsymbol{v}$ is uniform and constant, $\boldsymbol{v}(\boldsymbol{x}, t; \omega)$ is defined by (2.2), and the covariance tensor Γ_{ij} depends only on differences between space coordinates and time.

An important entity in the application of (2.8) is the Fourier transform of $\Gamma_{ij}(\boldsymbol{x}, t)$, denoted $S_{ij}(\boldsymbol{q},t)$. If $\psi_i(\boldsymbol{q}, t)$ represents the Fourier transform of $v_i(\boldsymbol{x}, t)$, then:

$$\langle\psi_i(\boldsymbol{q},t)\,,\psi_j(\boldsymbol{q}',t')\rangle = \delta(\boldsymbol{q}+\boldsymbol{q}')\,S_{ij}(\boldsymbol{q},t-t') \tag{3.3}$$

where $\delta(\boldsymbol{q})$ is a Dirac delta "function" (Sposito and Barry, 1987). Since $\boldsymbol{v}$ is uniform, the condition in (3.1) implies:

$$\boldsymbol{q}\cdot\psi(\boldsymbol{q},t;\omega) \equiv 0 \tag{3.4}$$

which can be used to show that:

$$\boldsymbol{q} \cdot \overline{\overline{S}} \cdot \boldsymbol{k} = \boldsymbol{k} \cdot \overline{\overline{S}} \cdot \boldsymbol{q} \equiv 0 \tag{3.5}$$

for arbitrary $\boldsymbol{k}$, where $\overline{\overline{S}}(\boldsymbol{q},t)$ is the tensor whose elements are $S_{ij}(\boldsymbol{q},t)$ [cf. Batchelor (1986, p. 27)]. Equation (3.4) also can be applied to (3.3) to help interpret it physically. The vector $\psi(\boldsymbol{q},t;\,\omega)$ can be decomposed quite generally into a component along $\boldsymbol{q}$ and one along a vector $\boldsymbol{b}$ in the plane perpendicular to $\boldsymbol{q}$:

$$\psi(\boldsymbol{q},t;\omega) = \psi \parallel (\boldsymbol{q},t;\omega)\hat{\boldsymbol{q}} + \psi \perp (\boldsymbol{q},t;\omega)\hat{\boldsymbol{b}} \tag{3.6}$$

where $\hat{\boldsymbol{b}}$ and $\hat{\boldsymbol{q}}$ are unit vectors and $\hat{\boldsymbol{b}} \cdot \hat{\boldsymbol{q}} \equiv 0$. The condition (3.4) implies $\psi \parallel \equiv 0$ and, therefore, that:

$$S_{ij}(\boldsymbol{q},t) = b_i b_j \langle \psi \perp (\boldsymbol{q},t)\, \psi \perp (-\boldsymbol{q},0)\rangle \tag{3.7}$$

according to (3.3) and (3.6). Equation (3.7) shows that the Fourier transform of the velocity covariance tensor depends only on the Fourier components of the velocity fluctuations that are perpendicular to $\boldsymbol{q}$.

In real space, the implication of (3.7) is that only the components of $\boldsymbol{v}(\boldsymbol{x},\,t;\,\omega)$ whose divergence vanishes identically are important to $\Gamma_{ij}(\boldsymbol{x} - \boldsymbol{x}',\, t - t')$. A well known theorem of vector calculus then can be invoked to express these components in terms of the curl of a vector potential which itself is expressible as a volume integral of the curl of the velocity component along $\boldsymbol{b}$ (cf. Gupta et al., 1977). If the solute velocity is described mathematically by the Buckingham-Darcy equation:

$$\boldsymbol{V}(\boldsymbol{x},t;\omega) = -K(\boldsymbol{x},t;\omega)\,\nabla\phi(\boldsymbol{x},t;\omega) \tag{3.8}$$

where K is a random hydraulic conductivity and ϕ is a random water potential (Dagan, 1984, 1987), then the curl of $\boldsymbol{V}$ is related directly to the spatial gradient of K (Gupta et al., 1977). The conclusion can be drawn from this conceptual analysis that spatial variability in K is connected intimately both with "vorticity" in $\boldsymbol{V}$ and with the Fourier component $\psi \perp (\boldsymbol{q},\, t;\, \omega)$ which appears in (3.7).

A simple model based on (3.8) can make this point more concrete. If the small random fluctuations in K and ϕ are denoted δK and $\delta\phi$, respectively, and if K and ϕ are uncorrelated random fields, then:

$$K \equiv \langle K\rangle + \delta K \qquad \nabla\phi \equiv \langle\nabla\phi\rangle + \nabla\delta\phi$$

$$\boldsymbol{v} = -\langle K\nabla\phi\rangle = -\langle K\rangle\langle\nabla\phi\rangle \tag{3.9}$$

and (2.2) can be combined with (3.8) to yield an expression for the velocity fluctuation:

$$\tilde{\boldsymbol{v}} = -\delta K\langle\nabla\phi\rangle - \langle K\rangle\nabla\delta\phi \approx \boldsymbol{v}\delta\ln K - \langle K\rangle\nabla\delta\phi \tag{3.10}$$

accurate to first order in the fluctuations. The Fourier transform of (3.10) is (in an infinite spatial domain):

$$\psi = \boldsymbol{v}\delta \ln \kappa - i\boldsymbol{q}\langle K\rangle\delta\varphi \tag{3.11}$$

where $\delta\kappa$ is the Fourier transform of δK and $\delta\varphi$ is that of $\delta\phi$. The application of (3.4) to (3.11) yields the condition:

$$\delta\varphi = -i\left(\frac{\boldsymbol{v}\cdot\boldsymbol{q}}{q^2}\right)\frac{\delta \ln \kappa}{\langle K\rangle} \tag{3.12}$$

so that (3.11) becomes:

$$\psi = [\boldsymbol{v} - (\boldsymbol{v}\cdot\hat{\boldsymbol{q}})\hat{\boldsymbol{q}}]\,\delta \ln \kappa \tag{3.13}$$

The corresponding component along the vector $\hat{\boldsymbol{b}}$ is:

$$b_1\psi \perp\approx [v_i - \hat{q}_i(\boldsymbol{v}\cdot\hat{\boldsymbol{q}})]\,\delta \ln \kappa \tag{3.14}$$

so that (3.7) becomes:

$$S_{ij}(\boldsymbol{q},t) \approx \left[v_i - \hat{q}_i(\boldsymbol{v}\cdot\hat{\boldsymbol{q}})\right]\left[v_j - \hat{q}_j(\boldsymbol{v}\cdot\hat{\boldsymbol{q}})\right]\langle\delta \ln \kappa(\boldsymbol{q},t)\,\delta \ln \kappa(-\boldsymbol{q},0)\rangle \tag{3.15}$$

Equation (3.15) is a model expression for an element of $\overline{\overline{S}}(\boldsymbol{q},t)$ in terms of the (uniform) mean solute velocity and the Fourier transform of the $\delta \ln \kappa$ covariance function. This model expression (with $t = 0$) has been used widely in applications (Dagan, 1987). It shows how fluctuations in the log hydraulic conductivity determine the covariance of $\hat{\boldsymbol{v}}(\boldsymbol{x},t;\omega)$ when (3.8) applies.

3.2. The ensemble-average transport equation

For a tracer solute, $y(\boldsymbol{x},t;\omega) = c(\boldsymbol{x},t;\omega)$ and the appropriate definitions of the operators A_0 and $A_1(t)$ are (Sposito and Barry, 1987):

$$A_0 \equiv (\nabla\cdot\overline{\overline{D}}\cdot\nabla - \boldsymbol{v}\cdot\nabla) \qquad A_1(t) = -\tilde{\boldsymbol{v}}(\boldsymbol{x},t;\omega)\cdot\nabla \tag{3.16}$$

where $\overline{\overline{D}}$ is a local (i.e., not field-scale) dispersion tensor. The resulting special case of (2.8) is complicated to write down entirely in real space, but Fourier transformation can be used to derive the relatively simple expression (Sposito and Barry, 1987; Kabala and Sposito, 1991):

$$\frac{\partial\langle c\rangle}{\partial t} = [\nabla\cdot(\overline{\overline{D}} + \overline{\overline{F}})\cdot\nabla]\langle c(\boldsymbol{x},t)\rangle - (\boldsymbol{v} - \boldsymbol{G})\cdot\nabla\langle c(\boldsymbol{x},t)\rangle \tag{3.17}$$

where:

$$\overline{\overline{F}}(t) \equiv \int_0^t \int \overline{\overline{S}}(\boldsymbol{q},t')\exp\left[-(\boldsymbol{q}\cdot\overline{\overline{D}}\cdot\boldsymbol{q})t'\right]\cos(\boldsymbol{v}\cdot\boldsymbol{q}t')\,\mathrm{d}q^3\,\mathrm{d}t' \tag{3.18}$$

$$G(t) \equiv \int_0^t \int (\overline{\overline{S}}(\boldsymbol{q},t') \cdot \boldsymbol{q}) \exp\left[-(\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q})t'\right] \sin(\boldsymbol{v} \cdot \boldsymbol{q}t')\, \mathrm{d}q^3 \mathrm{d}t' \tag{3.19}$$

with $G(t) = 0$ when (3.5) applies. Equation (3.17) has the form of a non-stochastic convection-dispersion equation, but it features the additional dispersion coefficient, $\overline{\overline{F}}(t)$. This additional coefficient arises solely from the solute velocity fluctuations occurring at field scales, as represented by the tensor $\overline{\overline{S}}(\boldsymbol{q},t)$.

Equation (3.18) embodies three time scales implicitly. One is that of the decay of $\overline{\overline{S}}(\boldsymbol{q},t)$, denoted τ_c, which is the time constant for temporal correlations in the fluctuations of the solute velocity to disappear. Another is $(\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q})^{-1}$, the time scale over which local dispersion takes place in a spatial region whose characteristic length is q^{-1}. A third is $(\boldsymbol{v} \cdot \boldsymbol{q})^{-1}$, the time scale for convection of the solute. Gelhar and Axness (1983) have studied (3.18) in the limit, $\tau_c \gg t \gg (\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q})^{-1}$, whereas Dagan (1984) has considered the opposite limit, $\tau_c \gg (\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q})^{-1} \gg t$. These two long-correlation-time models assume that the solute velocity fluctuations are "frozen" while the solute is propagated through the porous medium by local convection and dispersion. It is not difficult to show quite generally in this case that $\overline{\overline{F}}(t)$ will increase with time (initially at least) as the solute samples the static velocity fluctuations. These latter fluctuations are enormous compared to the pore-scale velocity fluctuations that produce $\overline{\overline{D}}$, so $\overline{\overline{F}}(t) \gg \overline{\overline{D}}$ after $t \approx \ell/v$, where ℓ is the length scale of the spatial velocity correlation (Sposito and Barry, 1987).

A simple model calculation will illustrate this point. Suppose that $\boldsymbol{v} = v\hat{\boldsymbol{x}}_1$ and that $S_{11}(\boldsymbol{q},t)$ depends only on q_3 because of stratification, with $\hat{\boldsymbol{x}}_3$ defining the vertical direction. Suppose further that the spatial velocity fluctuations are periodic along $\hat{\boldsymbol{x}}_3$ (a kind of regular stratification), so that $S_{11}(q_3,0) \propto \delta(q_3 \pm 2\pi/a)$, where a is the period of the fluctuations [cf. Güven and Molz (1986) and Sposito and Barry (1987)]. Then:

$$F_{11}(t) \propto \int_0^t \exp\left(\frac{-4\pi^2 D_{33} t'}{a^2}\right) \mathrm{d}t' = \frac{a^2}{4\pi^2 D_{33}}\left[1 - \exp\left(\frac{-4\pi^2 D_{33} t}{a^2}\right)\right] \tag{3.20}$$

which increases with time until $t \gg (a/2\pi)^2/D_{33}$, the local dispersion time scale.

4. Reactive solutes

4.1. Ensemble-average transport equations

The extension of (2.8) to reactive solutes is a straightforward application of the recipe developed in Section 3.2. Given a postulated stochastic differential equation like (1.2), an identification of sure and stochastic operators can be made, and a partial differential equation for the ensemble-average solute concentration can be derived which is analogous to (3.17) for a tracer solute (Kabala and Sposito,

TABLE 1

Specific examples of the sure operator A_0 and the stochastic operator $A_1(t)$ in (2.1)

Transport mechanisms	A_0	$A_1(t)$
Convection and dispersion	$\nabla \cdot \overline{\overline{D}} \cdot \nabla - \boldsymbol{v} \cdot \nabla$	$-\tilde{\boldsymbol{v}}(\boldsymbol{x}, t; \omega) \cdot \nabla$
Convection, dispersion and linear adsorption	$r\nabla \cdot \overline{\overline{D}} \cdot \nabla - \boldsymbol{u} \cdot \nabla$	$-\tilde{\boldsymbol{u}}(\boldsymbol{x}, t; \omega) \cdot \nabla$
Convection, dispersion and first-order decay	$\nabla \cdot \overline{\overline{D}} \cdot \nabla - \boldsymbol{v} \cdot \nabla - b$	$-\tilde{\boldsymbol{v}}(\boldsymbol{x}, t; \omega) \cdot \nabla - \tilde{b}(\boldsymbol{x})$

1991). Examples of the sure and stochastic operators that represent two kinds of reactive solute are presented in Table 1. For a solute that is transported by convection and local dispersion and which reacts with the solid matrix via linear adsorption/desorption on a time scale that is short compared with that for convection, the stochastic parameters are $\Re^{-1}(x; \omega)$, the inverse of the retardation factor, and $U(x, t; \omega) \equiv V(x, t; \omega) \Re^{-1}(x; w)$, the retarded velocity field. With the decomposition:

$$\Re^{-1}(x; \omega) = r + \tilde{r}(x; \omega) \qquad U(\boldsymbol{x}, t; \omega) = \boldsymbol{u} + \tilde{\boldsymbol{u}}(\boldsymbol{x}, t; \omega) \tag{4.1}$$

where $r = \langle \Re^{-1} \rangle$ and $\boldsymbol{u} = \langle U \rangle$ are uniform and constant mean values, the forms of the operators A_0 and $A_1(t)$ are determined as in Table 1. The resulting partial differential equation for $\langle c(\boldsymbol{x}, t) \rangle$ is then (Kabala and Sposito, 1991):

$$\begin{aligned} \frac{\partial \langle c \rangle}{\partial t} &= \left[\nabla \cdot (r\overline{\overline{D}} + \overline{\overline{F}}) \cdot \nabla \right] \langle c(\boldsymbol{x}, t) \rangle - (\boldsymbol{u} - \boldsymbol{G}) \cdot \nabla \langle c(\boldsymbol{x}, t) \rangle \\ &\quad + (\nabla \cdot \nabla \cdot \overline{\overline{A}} \cdot \nabla \cdot \nabla + \nabla \cdot \overline{\overline{E}} \cdot \nabla \cdot \nabla) \langle c(\boldsymbol{x}, t) \rangle \qquad (t > 0) \end{aligned} \tag{4.2}$$

where (with $\overline{\overline{F}}$ diagonal):

$$\begin{aligned} F_{ii} \equiv \int_0^t \int \mathrm{d}q^3 \exp(-r\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q}\tau) \cdot \Big\{ \Big[S_{ii}^{uu}(\boldsymbol{q}\tau) - D_{ii} \sum_j D_{jj} q_j^2 S^{rr}(\boldsymbol{q}) \Big] \cos(\boldsymbol{u} \cdot \boldsymbol{q}\tau) \\ - \sum_j [D_{jj} S_i^{ur}(\boldsymbol{q}, t - \tau) + D_{ii} S_j^{ur}(\boldsymbol{q}, t)] \, q_j \sin(\boldsymbol{u} \cdot \boldsymbol{q}\tau) \Big\} \, \mathrm{d}\tau \end{aligned} \tag{4.3}$$

$$G_i(t) \equiv \int_0^t \int \mathrm{d}q^3 \exp(-r\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q}\tau) \, q_i S_{ii}^{uu}(\boldsymbol{q}, \tau) \sin(\boldsymbol{u} \cdot \boldsymbol{q}\tau) \, \mathrm{d}\tau \tag{4.4}$$

$$A_{ij}(t) \equiv D_{ii} D_{jj} \int_0^t \int \mathrm{d}q^3 S^{rr}(\boldsymbol{q}) \exp(-r\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q}\tau) \cos(\boldsymbol{u} \cdot \boldsymbol{q}\tau) \, \mathrm{d}\tau \tag{4.5}$$

$$E_{ij}(t) \equiv \int_0^t \int \mathrm{d}q^3 \exp(-r\boldsymbol{q} \cdot \overline{\overline{D}} \cdot \boldsymbol{q}\tau) \cdot \{ 2D_{ii} D_{jj} S^{rr}(\boldsymbol{q}) \, q_i \sin(\boldsymbol{u} \cdot \boldsymbol{q}\tau)$$

$$- [D_{ii}S_j^{ur}(\boldsymbol{q},t-\tau) + D_{jj}S_i^{ur}(\boldsymbol{q},t)] \cos(\boldsymbol{u}\cdot\boldsymbol{q}\tau)\} \, \mathrm{d}\tau \tag{4.6}$$

under the assumption that $\overline{\overline{S}}(\boldsymbol{q},t)$ is a diagonal tensor. The first two terms on the right side of (4.2) are analogous to the right side of (3.17), but with the replacement of the tracer velocity by the retarded velocity. The last two terms arise because of correlations between the spatial fluctuations in $\Re^{-1}(\boldsymbol{x};\omega)$ and cross-correlations between $U(\boldsymbol{x},t;\omega)$ and $\Re^{-1}(\boldsymbol{x};\omega)$. They are of higher order in $\overline{\overline{D}}$ than the terms in $\overline{\overline{F}}$ or G and probably are less significant in the same way that the term in $r\overline{\overline{D}}$ is. [The functions $S^{rr}(q)$ and $S^{ur}(q,t)$ are Fourier transforms of covariance functions and are defined analogously to $S^{uu}(q,t)$ and $S_{ij}(q,t)$ in (3.3).]

For a solute that is transported by convection and dispersion while undergoing a first-order decay process, (2.2) and the stochastic decay constant:

$$B(\boldsymbol{x};\omega) = b + \tilde{b}(\boldsymbol{x};\omega) \tag{4.7}$$

are relevant to the construction of A_0 and $A_1(t)$ in Table 1. The resulting partial differential equation for the ensemble-average solute concentration is (Kabala and Sposito, 1991):

$$\frac{\partial\langle c\rangle}{\partial t} = (\nabla\cdot(\overline{\overline{D}}+\overline{\overline{F}})\cdot\nabla\langle c(\boldsymbol{x},t)\rangle - (\boldsymbol{v}-\boldsymbol{G})\cdot\nabla\langle c(\boldsymbol{x},t)\rangle$$

$$+ (b+H)\langle c(\boldsymbol{x},t)\rangle \qquad (t>0) \tag{4.8}$$

where $\overline{\overline{F}}$ and G are defined in (3.18) and (3.19) and:

$$H(t) \equiv \int_0^t \int \mathrm{d}q^3 \exp(-\boldsymbol{q}\cdot\overline{\overline{D}}\cdot\boldsymbol{q}\tau)$$

$$\left[S^{bb}(\boldsymbol{q})\cos(\boldsymbol{v}\cdot\boldsymbol{q}\tau) + \boldsymbol{q}\cdot S^{vb}(\boldsymbol{q},t)\sin(\boldsymbol{v}\cdot\boldsymbol{q}\tau)\right] \mathrm{d}\tau \tag{4.9}$$

with $S^{bb}(q)$ and $S^{vb}(q,t)$ defined analogously to $S^{ij}(q,t)$ in (3.3). In this example, the effects of velocity correlations produce the field-scale dispersion and convection parameters $\overline{\overline{F}}$ and G, while spatial correlations in $B(\boldsymbol{x};\omega)$ and cross-correlation between $B(\boldsymbol{x};\omega)$ and $V(\boldsymbol{x},t;\omega)$ lead to the field-scale decay parameter, $H(t)$. If (3.5) applies, G vanishes and H depends only on autocorrelation in $B(\boldsymbol{x};\omega)$.

4.2. Effective transport parameters

It is evident from the formal appearance of (3.17), (4.2) and (4.8) that the field-scale or "effective" solute convective velocity is either $\boldsymbol{v}-\boldsymbol{G}$ or $\boldsymbol{u}-\boldsymbol{G}$. This vector can be shown to be the same as the rate at which the solute plume center-of-mass moves through a porous medium (Kabala and Sposito, 1991). Similarly, the field-scale dispersion coefficient can be shown to be either $\overline{\overline{D}}+\overline{\overline{F}}$ or $r\overline{\overline{D}}+\overline{\overline{F}}$, equal to one-half the time-derivative of the second central spatial moment of $\langle c(\boldsymbol{x},t)\rangle$ (Freyberg, 1986; Kabala and Sposito, 1991).

For a linearly-adsorbing solute whose (stochastic) convective velocity is everywhere divergence-free, the effective velocity is the same as the ensemble average, $\langle \boldsymbol{V}R^{-1}\rangle$. This ensemble average in general is not equal to the quotient, $\langle \boldsymbol{V}\rangle/\langle R\rangle$, which sometimes is interpreted as the effective velocity of a linearly-adsorbing solute (Kabala and Sposito, 1991). The relation between the effective velocity and the tracer velocity $\boldsymbol{V}$ can be found readily for ensemble averages:

$$\langle \boldsymbol{V}\Re^{-1}\rangle = \boldsymbol{v}r + \langle \tilde{\boldsymbol{v}}(\boldsymbol{x},t)\,\tilde{r}(\boldsymbol{x})\rangle \tag{4.10}$$

Equation (4.10) is simply a rearrangement of the definition of the covariance function (Rao, 1984):

$$\begin{aligned}\operatorname{cov}(X,Y) &\equiv \langle XY\rangle - \langle X\rangle\langle Y\rangle\\ &= \langle \tilde{X}\tilde{Y}\rangle\end{aligned} \tag{4.11}$$

where X and Y are random variables. An important implication of (4.10) can be deduced by incorporating the definition of the field-scale retardation factor (Roberts et al., 1986):

$$R(t) \equiv \frac{\langle|\boldsymbol{V}|\rangle}{\langle|\boldsymbol{V}|\,\Re^{-1}\rangle} \tag{4.12}$$

The field-scale retardation factor is the ratio of tracer to physical solute velocities. An appeal to (4.10) applied to $|\boldsymbol{V}|$ shows that:

$$R(t) = r^{-1}\left\{1 - \left[\frac{\langle \tilde{v}(\boldsymbol{x},t)\,\tilde{r}(\boldsymbol{x})\rangle}{\langle V\,\Re^{-1}\rangle}\right]\right\} \tag{4.13}$$

In the absence of correlations between $|\boldsymbol{V}|$ and $\Re^{-1}$, the field-scale retardation factor will be uniform and constant, equal simply to the inverse of $\langle\Re^{-1}\rangle$. In the presence of correlations, and under the assumption of wide-sense stationarity, R will be uniform but time-dependent. If $|\boldsymbol{V}|$ and $\Re^{-1}$ are correlated negatively, then $R(t) > r^{-1}$, as has been observed in field studies of reactive organic solute movement through aquifers (Roberts et al., 1986).

5. Physical significance of the ensemble-average transport equation

5.1. The ensemble-average concentration

Partial differential equations like (3.17) are model results whose accuracy must be evaluated by comparison of the solution $\langle c(\boldsymbol{x},t)\rangle$ with experimentally-measured solute concentrations. Less sensitive tests of these equations, such as their predictions of spatial moments for a tracer plume (Freyberg, 1986; Barry and Sposito, 1990), are of heuristic value; but the ultimate validity of ensemble-average transport equations depends on the physical meaning of their fundamental variables and parameters. As outlined in Section 2.1, the concept of the ensemble-average solute concentration presupposes a hypothetical infinitude of identical porous media, over which an arithmetic average of solute concentrations at fixed points of space and time is performed to calculate $\langle c(\boldsymbol{x},t)\rangle$. If identical values of the concentration at the same position and time in different members of the ensemble are denoted with a single value of ω, then a knowledge of the probability density function for ω suffices to perform the averaging process.

The concentration variable appearing in (1.2) or (3.17) is formally a resident concentration (Kreft and Zuber, 1978; Sposito and Barry, 1987), which is defined as the mass of solute per unit volume of fluid contained in a volume element of a porous medium at a given time. This concentration variable figures directly in the balance of solute mass, and it is measurable locally if a fluid sample is withdrawn from a porous medium at a rate much larger than the solute convective velocity at the point of sampling. It is evident that the experimental resident solute concentration is always a volume average in the sense (Baveye and Sposito, 1984):

$$\bar{c}(\boldsymbol{x},t) \equiv \int c(\boldsymbol{x}+\xi,t)\, m(\xi,\boldsymbol{x},t)\, \mathrm{d}^3\xi \tag{5.1}$$

where $\boldsymbol{x}$ is the point in space associated with $\bar{c}$ and $m(\xi,\boldsymbol{x},t)$ is a "weighting function" whose mathematical properties depend on the experimental method used to measure the solute concentration. The integral in (5.1) is over all space, such that:

$$\int m(\xi,\boldsymbol{x},t)\, \mathrm{d}^3\xi = 1 \tag{5.2}$$

For example, if a cylinder of porous medium of volume V(x), radius R and altitude h is sampled to obtain the concentration:

$$m(\xi) = \begin{cases} (\pi R^2 h)^{-1} & \xi \in V(\boldsymbol{x}) \\ 0 & \xi \notin V(\boldsymbol{x}) \end{cases} \tag{5.3}$$

The physical quantity defined in (5.1) is to be related in some way to $\langle c(\boldsymbol{x},t)\rangle$ in (3.17), (4.2), or (4.8). Mathematical conditions under which an equality between $\langle c(\boldsymbol{x},t)\rangle$ and $\bar{c}(\boldsymbol{x},t)$ might be found have been discussed at length by Dagan (1984, 1987). If such an equality exists, $c(\boldsymbol{x},t;\omega)$ is said to be an "ergodic" stochastic process, but general postulates leading to its ergodicity are not known (Sposito et al., 1986). In an intuitive sense, it is evident that $\langle c(x,t)\rangle$ is unlikely to approximate $\bar{c}(\boldsymbol{x},t)$ very well unless the weighting function encompasses a large enough region of space to include all the possible variability in the solute concentration (at a given instant) that would be encountered in a survey of all members of the ensemble from which $\langle c(\boldsymbol{x},t)\rangle$ is calculated. Dagan (1987) has cited the pungent counter example of a tracer plume, comprising sinuous bands of solute separated by solute-free zones, which is sampled either in a band or in between bands to obtain $\bar{c}(\boldsymbol{x},t)$. These data will not be represented well by $\langle c(\boldsymbol{x},t)\rangle$, which must refer to an average of the two extremes.

5.2. The field-scale dispersion coefficient

Equation (3.17) exhibits a time-dependent, field-scale dispersion coefficient, $\overline{\overline{F}}(t)$, that is determined by correlations in space and time among the fluctuations in the solute velocity. The mathematical form of (3.17), as applied to some region of space, is that of an initial-value problem whose full solution requires a prescription of $\langle c(\boldsymbol{x},0)\rangle \equiv (\boldsymbol{x})$. As shown by Sposito and Barry (1987, equation 34) for the case of a factorizable $\langle c(\boldsymbol{x},t)\rangle$ in an infinite spatial domain [with (3.1) and (3.2) assumed]:

$$\langle c_i(x_i,t)\rangle = (4\pi\phi_i)^{-1/2} \int_{-\infty}^{\infty} f_i(\eta)\, \exp\left[\frac{-(x_i - v_i t - \eta)^2}{4\phi_i}\right] \mathrm{d}\eta \qquad (i = 1,2,3) \tag{5.4}$$

where:

$$\phi_i(t) \equiv \int_0^t [D_{ii} + F_{ii}(t')]\, \mathrm{d}t' \qquad (i = 1,2,3) \tag{5.5}$$

Equation (5.4) illustrates how the solute concentration depends on the initial spatial distribution of solute.

Neither (2.8) nor (3.17) is dependent on the absolute value of time: "time zero" is chosen arbitrarily and the variable t in these equations is elapsed time measured from this arbitrary reference, with the reference concentration taken as a sure function (cf. Dagan, 1984). Suppose that "time zero" is selected to be the instant, t_0, at which a tracer solute is injected into a porous medium, so that $f(\boldsymbol{x})$ is the initial configuration of the injected plume. At some $t_1 > t_0$, the plume concentrations are described by (5.4) with $t = t_1$. Now consider the possibility of injecting tracer into a second, identical porous medium with $f(\boldsymbol{x}) = \langle c(\boldsymbol{x},t_1)\rangle$ in the first medium. For this second medium, "time zero" corresponds to t_1 in the first medium, but the time evolution of $\langle c(\boldsymbol{x},t)\rangle$ should be the same if the two media are identical. Equation (5.5) can be applied to the second medium, but $f_i(\eta)$ and t are interpreted differently from in the first medium.

It follows also that $\phi_i(t)$ and, therefore, $\overline{\overline{F}}(t)$ will be different in the two porous media because the values of t are different, even though the values of $\langle c(\boldsymbol{x},t)\rangle$ are not. This situation is the logical end of the fact that (3.17) is an initial-value problem, and it would not be paradoxical except for the time-dependence of $\overline{\overline{F}}(t)$.

Since $\overline{\overline{F}}(t)$ changes with elapsed time, it is dependent on what initial condition is chosen with which to describe the solution of (3.17). That at t_0 cannot be favored as the "true" initial condition over that at t_1 because (3.17) does not depend on an absolute time. Thus different choices of initial condition in describing $\langle c(x,t)\rangle$ will produce differing values of the field-scale dispersion coefficient. Stated alternatively, the value of $\overline{\overline{F}}(t)$ will depend not only on intrinsic properties of the porous medium, but also on how the solute transport process is observed.

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