

# Macrodispersion of Sorbing Solutes in Heterogeneous Porous Formations With Spatially Periodic Retardation Factor and Velocity Field

CONSTANTINOS V. CHRYSIKOPOULOS,<sup>1</sup> PETER K. KITANIDIS, AND PAUL V. ROBERTS

*Department of Civil Engineering, Stanford University, Stanford, California*

Expressions for the macroscopic velocity vector and dispersion tensor for sorbing solute transport in heterogeneous porous formations whose hydrogeologic properties are repeated at intervals were derived via Taylor-Aris-Brenner moment analysis. An idealized three-dimensional porous formation of infinite domain with spatially periodic retardation factor, velocity field, and microdispersion coefficients in all three directions was considered. Sorption was assumed to be governed by a linear equilibrium isotherm under local chemical equilibrium conditions. The analytical expressions presented are based on a perturbation method where all of the spatially periodic parameters employed were assumed to have "small" fluctuations. It was shown that the effective velocity vector is given by the volume-averaged interstitial velocity vector divided by the volume-averaged retardation factor, and the effective dispersion dyadic (second-order tensor) is given by the volume-averaged microdispersion dyadic divided by the volume-averaged dimensionless retardation factor plus a dyadic expressing the increase in solute spreading caused by the spatial variability of the parameters.

## INTRODUCTION

Macroscopically, spreading of conservative nonreacting solutes in the subsurface is caused primarily by variable rates of advective transport of the interstitial fluid due to natural spatial variability of conductivity [Dagan, 1989]. The macroscopic property of the porous medium which characterizes the rate of spreading is known as dispersivity. At a laboratory or pore scale, dispersivity is often considered constant, with values of the order of a few grain diameters, and solute dispersion is assumed to be Fickian, i.e., the dispersive flux is proportional to the concentration gradient. At a field or local scale, as has been found in field tests [e.g., Sauty, 1980; Domenico and Robbins, 1984; Freyberg, 1986; Sudicky, 1986; Garabedian et al., 1988], the observed dispersivity increases with distance from the solute injection point along the flow path until, for some cases, it seems to converge to a maximum asymptotic value. In the transient or preasymptotic zone the solute plume readjusts to the variations in hydraulic conductivity. Field-scale dispersivities are much larger than pore-scale dispersivities [Fried and Combarous, 1971; Pickens and Grisak, 1981], and solute dispersion at the field scale is not critically affected by variations in pore-scale dispersivities [Vomvoris, 1986].

The macrodispersion of nonreacting conservative solutes or tracers in heterogeneous subsurface formations has been the focus of several theoretical investigations. Schwartz [1977] and Smith and Schwartz [1980, 1981] employed Monte Carlo techniques to show that the dispersivity may not converge to a maximum asymptotic value in a finite, two-dimensional porous medium with spatially variable hydraulic conductivity, represented as a realization of a stationary random field. Gelhar et al. [1979] and Matheron and de Marsily [1980] found that the assumption of Fickian macrodispersion is not valid for the special case of solute transport

in perfectly stratified aquifers with layers of random permeability and unidirectional flow field parallel to the stratification. Gillham et al. [1984] developed a conceptual advection-diffusion model for solute transport in stratified formations consisting of high/low permeability layers allowing for inter-layer mass transfer under unidirectional flow parallel to bedding. They concluded that solute macrodispersion is not Fickian under these conditions. Güven et al. [1984] have shown that, in stratified formations with hydraulic conductivities that are known functions of the vertical coordinate, macrodispersivities become asymptotically Fickian when the flow domain has finite thickness and is contained between impermeable boundaries at the top and the bottom. Gelhar and Axness [1983], Dagan [1982a, 1984, 1987, 1988] and Neuman et al. [1987] employed different analytical approaches to derive expressions for Fickian macrodispersivity coefficients which depend on the mean flow gradient and the statistics of the log hydraulic conductivity field. This analysis is for stationary conductivity and large Peclet numbers, and is exact at the limit when the conductivity fluctuations are small. Gupta and Bhattacharya [1986] derived macrodispersion coefficients for solute transport in porous media with spatially periodic velocity field. Kitanidis [1988] derived general expressions for the first two spatial moments of solute concentration in heterogeneous porous media with random but time-invariant flow velocities, and microdispersion coefficients. Neuman and Zhang [1990] and Zhang and Neuman [1990] developed a quasi-linear theory which accounts for both non-Fickian and Fickian dispersion in subsurface formations. Neuman [1990] has shown that a fractal model of log hydraulic conductivity is consistent with the observed scale effect in dispersion coefficients.

All of the previously described studies provided valuable information for improving the description and prediction of nonreacting conservative solute or tracer transport in heterogeneous formations. However, it is difficult to assess these theories, because the ideal conservative tracer may not exist [Davis et al., 1980]. Furthermore, the attention of hydrogeologists and environmental engineers is currently focused on the transport of sorbing or reacting toxic contaminants in natural subsurface porous media, an area of great practical

<sup>1</sup> Now at Department of Civil Engineering, University of California, Irvine.

importance. Laboratory [Durant and Roberts, 1986] and field [Elabd, 1984; Muckay et al., 1986a; Roberts et al., 1986] solute transport investigations suggest that sorption is spatially variable. Therefore, mathematical models for sorbing solute transport in subsurface porous media should not consider the retardation factor as a position-independent constant, but rather as a spatially variable parameter. Chrysikopoulos et al. [1990a] developed an analytical stochastic sorbing solute transport model for one-dimensional homogeneous porous media to demonstrate that spatially variable retardation increases the solute spreading. Valocchi [1989] employed the classical Taylor-Aris dispersion analysis to derive expressions for the asymptotic macrodispersion coefficients of kinetically sorbing solute transport through perfectly stratified formations. Garabedian et al. [1988] employed spectral small-perturbation methods to analyze reactive solute macrodispersion under the assumption that the log hydraulic conductivity is linearly related to both porosity and the distribution coefficient. Their results indicate that solute spreading is enhanced when there is negative correlation between the log hydraulic conductivity and the distribution coefficient. Chrysikopoulos et al. [1992] derived expressions for the macroscopic velocity vector and the dispersion dyadic for sorbing solute transport under local equilibrium as well as first-order reversible sorption conditions in three-dimensional homogeneous porous media, where the retardation factor was assumed spatially periodic in all three directions and the flow field unidirectional.

The goal of this work is to derive expressions for the effective or macroscopic transport coefficients for a solute sorbing under local equilibrium conditions in a heterogeneous porous medium with a retardation factor, a velocity field, and microdispersion coefficients that are spatially periodic in all three directions. The effective coefficients governing the macroscopic solute transport can be employed in the advection-dispersion equation with effective coefficients to predict the transport of a sorbing solute after enough time has elapsed for the plume to spread out over an area larger than the scale of fluctuations of the interstitial fluid velocity and the retardation factor. Thus, a heterogeneous porous formation with spatially variable geochemical properties may be represented by an equivalent porous formation with homogeneous hydrogeochemical characteristics. The results of this study provide physical insights which improve our understanding of what macroscopic coefficients really signify.

The spatially periodic model for heterogeneous porous media employed in this investigation allows averaging of the local-scale variability via the generalized Taylor-Aris moment analysis [Brenner, 1980a, 1982a, b]. An alternative approach for the elimination of the local space dependence entails homogenization techniques [Bensoussan et al., 1978], as have been employed by Rubinstein and Mauri [1986] and Rubinstein and Torquato [1989]. The periodic model is a mathematical idealization appropriate for cases where parameter fluctuations are characterized by the absence of well-defined secular trends and resemble the superposition of many waves of variable wavelength and displacement. Such variability is best described through spectra, which measure the amplitude and phase of the waves that form the variable parameter versus the wavelength. The periodic model is no more unrealistic than the frequently used infinite and semi-infinite models of porous media [e.g., Lindstrom et

al., 1967; van Genuchten et al., 1984; Goltz and Roberts, 1986; Chrysikopoulos et al., 1990a, b; Yates, 1990].

Although porous media with periodic hydrogeochemical parameters are not observed in nature, the macrodispersion coefficients derived in this work by the periodic model are applicable to variability scales smaller than the periodicity. The results can be extended to the case of stationary random media by sufficiently increasing the period of the periodic model. Such mathematical development is beyond the scope of this paper.

## PROBLEM FORMULATION

Consider a three-dimensional porous formation with spatially periodic interstitial velocity and geochemical parameters in all three directions. Assuming that all periodic parameters vary in each principal direction of a Cartesian coordinate system with identical spatial period  $l_x$ ,  $l_y$ , and  $l_z$  respectively, the porous formation may be divided into identical rectangular parallelepiped elements with edges defined by the vectors  $\mathbf{l}_x$ ,  $\mathbf{l}_y$ , and  $\mathbf{l}_z$  (e.g.,  $\mathbf{l}_y = (0, l_y, 0)^T$ ). A vector of spatial coordinates  $\mathbf{Q} = (Q_x, Q_y, Q_z)^T$  may be written as the sum of an unbounded global variable  $\mathbf{Q}_n = (Q_{n_x}, Q_{n_y}, Q_{n_z})^T$  and a bounded local variable  $\mathbf{q}$  [Brenner, 1980b; Brenner and Adler, 1982]. Explicitly,

$$\mathbf{Q} = \mathbf{Q}_n + \mathbf{q}, \quad (1)$$

where

$$\mathbf{Q}_n = \begin{pmatrix} n_x l_x \\ n_y l_y \\ n_z l_z \end{pmatrix} \quad (2a)$$

$$\mathbf{q} = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} \quad (2b)$$

$$n_i = 0, \pm 1, \pm 2, \pm 3, \dots \quad (i = x, y, z), \quad (3)$$

$$0 \leq q_i \leq l_i, \quad (4)$$

and the subscript  $\mathbf{n}$  denotes the  $n$ th unit element which is defined by the triplet of integers:  $\{\mathbf{n}\} = \{n_x, n_y, n_z\}$ .  $\mathbf{Q}_n$  locates the origin of the  $n$ th unit element and  $\mathbf{q}$  specifies a local point within the  $n$ th unit element.

The transport of a sorbing solute through a three-dimensional heterogeneous porous formation under steady state flow conditions is governed by the following partial differential equation:

$$\frac{\partial C(t, \mathbf{Q})}{\partial t} + \frac{\rho}{\theta} \frac{\partial C^*(t, \mathbf{Q})}{\partial t} = \nabla_{\mathbf{q}} \cdot [\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} C(t, \mathbf{Q}) - \mathbf{U}(\mathbf{q})C(t, \mathbf{Q})], \quad (5)$$

where  $C(t, \mathbf{Q})$ , which can also be written as  $C(t, \mathbf{Q}_n, \mathbf{q})$ , is the volume-averaged or resident liquid phase solute concentration, which is defined as the solute mass per unit volume of interstitial fluid, as opposed to the flux-averaged concentration which corresponds to the solute mass per unit volume of fluid flowing through a given cross section per unit time,  $C^*(t, \mathbf{Q})$  is the solid phase or sorbed solute concentration defined as the sorbed solute mass per aquifer solids mass,

$\mathbf{D}(\mathbf{q})$  is a symmetric matrix of the hydrodynamic microdispersion or local dispersion coefficients,  $\mathbf{U}(\mathbf{q})$  is the nondivergent steady state interstitial fluid velocity vector (incompressible fluid), which satisfies the condition

$$\nabla_{\mathbf{q}} \cdot \mathbf{U}(\mathbf{q}) = 0; \quad (6)$$

$t$  is time,  $\rho$  is the bulk density of the solid matrix,  $\theta$  is porosity,  $\nabla_{\mathbf{q}}$  is the vector differential operator ( $\nabla_{\mathbf{q}} = [\partial/\partial q_x, \partial/\partial q_y, \partial/\partial q_z]^T$ ),  $\nabla_{\mathbf{q}} \cdot \mathbf{F}$  denotes divergence ( $\nabla_{\mathbf{q}} \cdot \mathbf{F} = \partial F_x/\partial q_x + \partial F_y/\partial q_y + \partial F_z/\partial q_z$ ); and  $\mathbf{F}$  is an arbitrary function.

For linear, reversible, instantaneous sorption, the equilibrium relationship between the solute substance in the aqueous and solid phases is given by

$$C^*(t, \mathbf{Q}) = K_d(\mathbf{q})C(t, \mathbf{Q}), \quad (7)$$

where  $K_d(\mathbf{q})$  is the partition or distribution coefficient, defined as the ratio of solute concentration on the adsorbent to solute aqueous concentration at equilibrium. Alternatively, the equilibrium relationship (7) can be written as

$$S^*(t, \mathbf{Q}) = k_d(\mathbf{q})C(t, \mathbf{Q}), \quad (8)$$

where

$$S^*(t, \mathbf{Q}) = \frac{\rho C^*(t, \mathbf{Q})}{\theta} \quad (9)$$

is the solid phase or sorbed solute concentration with units identical to  $C(t, \mathbf{Q})$ , and

$$k_d(\mathbf{q}) = \frac{\rho K_d(\mathbf{q})}{\theta} \quad (10)$$

is the dimensionless partition or distribution coefficient. Combining (5) and (8) leads to

$$R(\mathbf{q}) \frac{\partial C(t, \mathbf{Q})}{\partial t} = \nabla_{\mathbf{q}} \cdot [\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} C(t, \mathbf{Q}) - \mathbf{U}(\mathbf{q})C(t, \mathbf{Q})], \quad (11)$$

where the dimensionless variable  $R(\mathbf{q})$  is the retardation factor defined as

$$R(\mathbf{q}) = 1 + k_d(\mathbf{q}). \quad (12)$$

For an unbounded porous formation in which the solute is initially absent and the solute mass is instantaneously injected at  $t = 0$  at the point  $\mathbf{Q}^0 = \mathbf{Q}_{n^0} + \mathbf{q}^0$ , the appropriate initial and boundary conditions are

$$C(0, \mathbf{Q}) = W\delta(\mathbf{Q} - \mathbf{Q}^0) = W\delta_{nn^0}\delta(\mathbf{q} - \mathbf{q}^0), \quad (13)$$

$$\lim_{\|\mathbf{Q} - \mathbf{Q}^0\| \rightarrow \infty} C(t, \mathbf{Q}) = \lim_{\|\mathbf{Q}_n - \mathbf{Q}_{n^0}\| \rightarrow \infty} C(t, \mathbf{Q}) = 0, \quad (14)$$

where  $W$  is the injected solute mass;  $\delta_{nn^0}$  is the Kronecker delta for unit elements  $\mathbf{n}$  and  $\mathbf{n}^0$  ( $\delta_{nn^0} = \delta_{n_x n_x^0} \delta_{n_y n_y^0} \delta_{n_z n_z^0}$ ); and  $\delta(\mathbf{q} - \mathbf{q}^0)$  is a Dirac delta function. Note that  $C^*(0, \mathbf{Q}) = 0$  and  $\delta_{nn^0}\delta(\mathbf{q} - \mathbf{q}^0) = \delta(\mathbf{Q} - \mathbf{Q}^0)$ . The first equality in condition (14) holds, because  $\|\mathbf{q} - \mathbf{q}^0\| = O(l_i)$  [Brenner, 1980b]. The solute concentration can also be interpreted as a probability density function provided that  $W = 1$ :  $C(t, \mathbf{Q}_n, \mathbf{q}|\mathbf{Q}_{n^0}, \mathbf{q}^0) = C(t, \mathbf{Q}_n - \mathbf{Q}_{n^0}, \mathbf{q}|\mathbf{q}^0)$  [Brenner, 1980a, b].

Hereafter, for notational convenience it is assumed that  $\mathbf{Q}_{n^0} = \mathbf{0}$  and  $\mathbf{q}^0 = \mathbf{0}$ , where  $\mathbf{0}$  is the null vector and indicates the unit element defined by  $\{\mathbf{n}^0\} = \{0, 0, 0\}$ . Furthermore, we impose the conditions that the solute concentration and the dispersive flux are continuous on each interface,  $\partial\mathbf{q}_i$ , of a unit element [Brenner, 1980b; Shapiro and Brenner, 1988]:

$$C(t, \mathbf{Q}_n, \mathbf{q}) = C(t, \mathbf{Q}_n - \mathbf{l}_i, \mathbf{q} + \mathbf{l}_i) \quad (\mathbf{q} \in \partial\mathbf{q}_i), \quad (15)$$

$$\nabla_{\mathbf{q}} C(t, \mathbf{Q}_n, \mathbf{q}) = \nabla_{\mathbf{q}} C(t, \mathbf{Q}_n - \mathbf{l}_i, \mathbf{q} + \mathbf{l}_i) \quad (\mathbf{q} \in \partial\mathbf{q}_i). \quad (16)$$

In the present analysis, the retardation factor, the velocity field, and consequently the microdispersion coefficients are modeled as periodic with the same directional spatial periods  $l_x$ ,  $l_y$ , and  $l_z$ , which means that for any  $\mathbf{q}$  in the interior or the boundary of the unit element ( $\mathcal{B} = R, U, D$ )

$$\mathcal{B}(\mathbf{q}) = \mathcal{B}(\mathbf{q} + \mathbf{l}_i). \quad (17)$$

$R(\mathbf{q})$ ,  $\mathbf{U}(\mathbf{q})$ , and  $\mathbf{D}(\mathbf{q})$ , as well as their derivatives, are also continuous at any point on the six faces of each parallelepiped unit element:

$$\mathcal{B}(\mathbf{Q}_n, \mathbf{q}) = \mathcal{B}(\mathbf{Q}_n - \mathbf{l}_i, \mathbf{q} + \mathbf{l}_i) \quad (\mathbf{q} \in \partial\mathbf{q}_i), \quad (18)$$

$$\nabla_{\mathbf{q}} \mathcal{B}(\mathbf{Q}_n, \mathbf{q}) = \nabla_{\mathbf{q}} \mathcal{B}(\mathbf{Q}_n - \mathbf{l}_i, \mathbf{q} + \mathbf{l}_i) \quad (\mathbf{q} \in \partial\mathbf{q}_i). \quad (19)$$

Note that in (15), (16), (18) and (19), the vector  $\mathbf{q}$  is on an interface of two consecutive unit elements.

#### SPATIAL MOMENTS

In order to obtain the expressions for the asymptotic coefficients governing the macroscopic solute transport, the generalized approach [Brenner, 1980a, 1982a, b; Dill and Brenner, 1982a, b; Frankel and Brenner, 1989] to the original method of moments [Taylor, 1953, 1954; Aris, 1956] is employed. In the context of the generalized theory of Taylor-Aris-Brenner dispersion theory, the local spatial moments of the liquid phase solute concentration are defined as

$$\mathbf{m}_m(t, \mathbf{q}) = \sum_{\mathbf{n}} \mathbf{Q}_n^m C(t, \mathbf{Q}_n, \mathbf{q}) \quad (20)$$

$$(m = 0, 1, 2, \dots),$$

where

$$\sum_{\mathbf{n}} \stackrel{\text{def}}{=} \sum_{n_x = -\infty}^{\infty} \sum_{n_y = -\infty}^{\infty} \sum_{n_z = -\infty}^{\infty} \quad (21)$$

$\mathbf{Q}_n^m = \mathbf{Q}_n \cdots \mathbf{Q}_n$  ( $m$  times) is an  $m$ -adic. Thus  $\mathbf{Q}_n^0 = 1$ ;  $\mathbf{Q}_n^1 = \mathbf{Q}_n$ ;  $\mathbf{Q}_n^2$  is the second-order tensor (dyadic) whose  $ij$ th element is the product of the  $i$  and  $j$  element of  $\mathbf{Q}_n$ ; and so on. The zeroth local moment ( $m_0$ ) is a scalar and represents the sum of concentrations at all points with local coordinates  $\mathbf{q}$ ; the first local moment ( $\mathbf{m}_1$ ) is a vector whose  $i$ th element can be written as  $m_{1(i)} = \sum_{\mathbf{n}} Q_n C(t, \mathbf{Q}_n, \mathbf{q})$ ; and the second local moment ( $\mathbf{m}_2$ ) is a symmetrical dyadic whose  $ij$ th element can be written as  $m_{2(ij)} = \sum_{\mathbf{n}} Q_n Q_n C(t, \mathbf{Q}_n, \mathbf{q})$ .

The global moments of the liquid phase solute concentration are defined as

$$\mathbf{M}_m(t) = \int_{V_0} \mathbf{m}_m(t, \mathbf{a}) d^3\mathbf{a}. \quad (22)$$

where  $V_0$  is the domain of a unit element and  $d^3\mathbf{q}$  is a differential volume within a unit element. The zeroth global moment ( $M_0$ ) is a scalar and represents the total mass in solution; the first moment ( $\mathbf{M}_1$ ) is a vector and  $\mathbf{M}_1/M_0$  indicates the position of the center of mass; the second moment ( $\mathbf{M}_2$ ) is a dyadic and  $\mathbf{M}_2/M_0$  measures the mean square displacement of the plume, after averaging the solute concentration within each element, about the origin of the  $n^{\text{th}}$  unit element where solute was introduced instantaneously as a point source. Similarly, the local moments for the solid phase or sorbed solute concentration,  $\mathbf{p}_m(t, \mathbf{q})$ , are obtained by replacing  $C(t, \mathbf{Q}_n, \mathbf{q})$  for  $S^*(t, \mathbf{Q}_n, \mathbf{q})$  in (20), whereas the global moments  $\mathbf{P}_m(t)$  are obtained by integrating  $\mathbf{p}_m(t, \mathbf{q})$  over the volume of a unit element.

The rate of change of the local moments of the liquid phase solute concentration is obtained by rewriting the parabolic partial differential equation (11) in terms of local coordinates, multiplying the resulting equation by  $\mathbf{Q}_n^m$  and then summing over all unit elements. Explicitly,

$$\sum_n \mathbf{Q}_n^m \left\{ R(\mathbf{q}) \frac{\partial C(t, \mathbf{Q}_n, \mathbf{q})}{\partial t} - \nabla_{\mathbf{q}} \cdot [\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} C(t, \mathbf{Q}_n, \mathbf{q}) - \mathbf{U}(\mathbf{q})C(t, \mathbf{Q}_n, \mathbf{q})] \right\} = 0. \quad (23)$$

Since  $R(\mathbf{q})$ ,  $\mathbf{U}(\mathbf{q})$  and  $\mathbf{D}(\mathbf{q})$  are independent of  $\mathbf{n}$ , (23) may be written as

$$R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} = \nabla_{\mathbf{q}} \cdot [\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \mathbf{m}_m - \mathbf{U}(\mathbf{q})\mathbf{m}_m]. \quad (24)$$

In addition to (24), the local moments satisfy certain boundary conditions imposed at the unit element surfaces. These conditions are derived from (15), (16) and (20) and are expressed in terms of "local jumps" as follows [Brenner, 1980b; Brenner and Adler, 1982; Dill and Brenner, 1982a, b, 1983; Shapiro and Brenner, 1988]:

$$[[m_0]] = 0 \quad (25a)$$

$$[[\nabla_{\mathbf{q}} m_0]] = 0; \quad (25b)$$

$$[[\mathbf{m}_1]] = -[[\mathbf{q}m_0]] \quad (26a)$$

$$[[\nabla_{\mathbf{q}} \mathbf{m}_1]] = -[[\nabla_{\mathbf{q}} (\mathbf{q}m_0)]]; \quad (26b)$$

$$[[\mathbf{m}_2]] = \left[ \frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right] \quad (27a)$$

$$[[\nabla_{\mathbf{q}} \mathbf{m}_2]] = \left[ \nabla_{\mathbf{q}} \left( \frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right) \right]. \quad (27b)$$

The local jump term  $[[\mathbf{F}]]$  indicates the difference between the values of the function  $\mathbf{F}$  at equivalent points on opposite faces of a unit element, i.e.,

$$[[\mathbf{F}]] = \mathbf{F}(\mathbf{q} + \mathbf{l}_i) - \mathbf{F}(\mathbf{q}) \quad (\mathbf{q} \in \partial \mathbf{q}_i), \quad (28)$$

where  $\mathbf{F}$  is an arbitrary function of local coordinates.

The local moments for the solid phase solute concentration are obtained in a similar fashion by rewriting the equilibrium relationship (8) in terms of local coordinates,

multiplying the resulting equation by  $\mathbf{Q}_n^m$  and then summing over all unit elements. Explicitly,

$$\mathbf{p}_m = k_d(\mathbf{q})\mathbf{m}_m \quad (29)$$

is the linear relationship between the local moments for the liquid and solid phase solute concentration.

Integrating both sides of (24) over the domain of a unit element and applying the divergence theorem on the right-hand side leads to

$$\int_{V_0} R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} d^3\mathbf{q} = \int_{\partial V_0} [\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \mathbf{m}_m - \mathbf{U}(\mathbf{q})\mathbf{m}_m] \cdot \mathbf{n}_s ds, \quad (30)$$

where  $\partial V_0$  is the external surface area of a unit element,  $\mathbf{n}_s$  is the outer unit vector normal to  $\partial V_0$ , and  $ds$  is an infinitesimal surface area on  $\partial V_0$ . A surface integral over the area of a unit element can be written in terms of local jumps as [Brenner, 1980b]

$$\int_{\partial V_0} \mathbf{F} \cdot \mathbf{n}_s ds = \sum_i \int_{s_{\pm i}} [[\mathbf{F}]] \cdot \mathbf{n}_s ds, \quad (31)$$

where  $s_{\pm i}$  ( $s_{+i} = s_{-i}$ ) denotes the faces of the unit element, while the plus or minus sign permits identification of equivalent but opposite faces. Substitution of the preceding identity into (30) yields

$$\int_{V_0} R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} d^3\mathbf{q} = \sum_i \int_{s_{\pm i}} \{ [[\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \mathbf{m}_m] - [[\mathbf{U}(\mathbf{q})\mathbf{m}_m]] \} \cdot \mathbf{n}_s ds, \quad (32)$$

which is suitable for direct application of jump boundary conditions (25)–(27).

#### LARGE-TIME BEHAVIOR

This section is devoted to the derivation of the zeroth, first and second global moments for the three-dimensional transport problem considered. It is important to distinguish the difference between local and global moments, and to note that the  $m$ th global moment depends on the first  $m - 1$  local moments. The local moments are determined sequentially by solving the boundary value problems described by (24)–(27), whereas the global moments are obtained by integrating the derived local moments over the volume of a unit element. All moments are determined under the assumption that the plume is spread out enough so that the zero local moment is constant, or equivalently, that the sum of concentrations at all points with local coordinates  $\mathbf{q}$  is independent of time and location within the unit element.

#### Zero-Order Moments

At large values of time, for  $m = 0$ , the solution to (24) subject to jump boundary conditions (25a) and (25b) is by inspection deduced to be

$$m_0 = \text{const.} \quad (33)$$

The preceding equation indicates that a steady state has been reached for  $m_0$ , and does not generally imply that the solute concentration is also at a steady state. Equation (33) becomes valid when the plume extends over several unit elements, which certainly does not mean that the concentration has reached steady state. Since the solute introduced into the porous formation is sorbing but otherwise nonreacting, the total liquid phase solute mass is not equal to the injected mass for all time, but depends critically on the spatial periodicity of sorption. However, the conservation of mass law requires that the sum of the zero-order global moments for liquid phase and sorbed solute concentration is at all time equal to the mass injected,

$$M_0 + P_0 = W. \quad (34)$$

In view of (12), (29) and (34) the zero-order local moment for the liquid phase solute concentration may be written as

$$m_0 = \frac{W}{l_x l_y l_z \bar{R}} = \frac{W}{V_0 \bar{R}}, \quad (35)$$

where the dimensionless variable

$$\bar{R} \stackrel{\text{def}}{=} \frac{1}{V_0} \int_{V_0} R(\mathbf{q}) d^3 \mathbf{q}, \quad (36)$$

is the retardation factor averaged over the volume of a unit element. Integrating  $m_0$  over the volume of a unit element yields the liquid phase zero-order global moment

$$M_0 = \frac{W}{\bar{R}}. \quad (37)$$

*First-Order Moments*

For  $m = 1$ , (32) can be written as

$$\int_{V_0} R(\mathbf{q}) \frac{\partial \mathbf{m}_1}{\partial t} d^3 \mathbf{q} = \sum_i \int_{s_{i-1}}^{s_i} \{ -[\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}}(\mathbf{q}m_0)] + [U(\mathbf{q})\mathbf{q}m_0] \} \cdot \mathbf{n}_x ds, \quad (38)$$

where the local unit element boundary conditions (26a) and (26b) have been employed. For the  $m_{1(i)}$  element of the first local moment vector, where the subscripts in parentheses indicate the appropriate elements of the corresponding vector  $\mathbf{m}_1$ , (38) can be written as follows:

$$\int_{V_0} R(\mathbf{q}) \frac{\partial m_{1(i)}}{\partial t} d^3 \mathbf{q} = \frac{W \bar{U}_x}{\bar{R}}, \quad (39)$$

where

$$\bar{U}_x \stackrel{\text{def}}{=} \frac{1}{V_0} \int_{V_0} U_x(\mathbf{q}) d^3 \mathbf{q}, \quad (40)$$

and the dispersion term in (38) is eliminated because  $[\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}}(\mathbf{q}m_0)] = m_0[\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}}\mathbf{q}]$  is equal to zero.

Inspection of boundary conditions (26a) and (26b) suggests that for large times a trial solution for  $m_{1(i)}$  is of the form

$$m_{1(i)} = [\Gamma_x t - q_x + \Phi_x(\mathbf{q})]m_0, \quad (41)$$

where  $\Gamma_x$  is a constant and  $\Phi_x(\mathbf{q})$  is a function of the local coordinates with symmetric values on the boundary of the unit element. That is,

$$\Phi_x(\mathbf{q}) = \Phi_x(\mathbf{q} + \mathbf{l}_i) \quad (\mathbf{q} \in \partial \mathbf{q}_i), \quad (42)$$

$$\nabla_{\mathbf{q}} \Phi_x(\mathbf{q}) = \nabla_{\mathbf{q}} \Phi_x(\mathbf{q} + \mathbf{l}_i) \quad (\mathbf{q} \in \partial \mathbf{q}_i). \quad (43)$$

Note that (41) satisfies the conditions (26a) and (26b). Substituting (41) into (39) the constant  $\Gamma_x$  is easily evaluated to be

$$\Gamma_x = \frac{\bar{U}_x}{\bar{R}}. \quad (44)$$

Combining (44) and (41), the general trial solution for any element  $m_{1(i)}$  is given by

$$m_{1(i)} = \left[ \frac{\bar{U}_i t}{\bar{R}} - q_i + \Phi_i(\mathbf{q}) \right] m_0 \quad (i = x, y, z). \quad (45)$$

Employing (22) and (45) yields the expression for the elements of the first global moment,

$$M_{1(i)} = \left[ \frac{\bar{U}_i t}{\bar{R}} - \frac{l_i}{2} + \bar{\Phi}_i \right] \frac{W}{\bar{R}}, \quad (46)$$

where

$$\bar{\Phi}_i \stackrel{\text{def}}{=} \frac{1}{V_0} \int_{V_0} \Phi_i(\mathbf{q}) d^3 \mathbf{q}. \quad (47)$$

To complete the description of the first-order local moments,  $\Phi_i(\mathbf{q})$  must be determined. Since  $\Phi_i(\mathbf{q})$  is periodic it can be expanded in the following Fourier series

$$\Phi_i(\mathbf{q}) = \bar{\Phi}_i + \Phi_i'(\mathbf{q}) = \bar{\Phi}_i + \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq 0}} \mu_i(\mathbf{b}) \exp [j2\pi \mathbf{q} \cdot \mathbf{b}], \quad (48)$$

where the prime signifies fluctuations,  $j = (-1)^{1/2}$ ,  $\mathbf{b}$  is a three-dimensional vector of integers,  $\mathbf{b} = (b_x, b_y, b_z)^T = (b_x/l_x, b_y/l_y, b_z/l_z)^T$ , and the expression for the coefficients  $\mu_i(\mathbf{b})$  is derived in Appendix A by the method of small perturbations or first-order approximation,

$$\mu_i(\mathbf{b}) = \frac{\nu_i(\mathbf{b}) - \frac{\bar{U}_i}{\bar{R}} \lambda(\mathbf{b}) - j2\pi \xi_i(\mathbf{b}) \cdot \mathbf{b}}{4\pi^2 \mathbf{b} \cdot \bar{\mathbf{D}} \cdot \mathbf{b} + j2\pi \bar{U} \cdot \mathbf{b}}, \quad (49)$$

where  $\lambda(\mathbf{b})$  is a scalar defined in (A6),  $\nu(\mathbf{b})$  is a vector defined in (A7),  $\xi(\mathbf{b})$  is a symmetric matrix of known coefficients defined in (A8),  $\nu_i(\mathbf{b})$  is the  $i$ th element of  $\nu(\mathbf{b})$ , and  $\xi_i(\mathbf{b})$  is the  $i$ th column of  $\xi(\mathbf{b})$ .

*Second-Order Moments*

For  $m = 2$ , (32) can be written as

$$\int_{V_0} R(\mathbf{q}) \frac{\partial \mathbf{m}_2}{\partial t} d^3 \mathbf{q} = \sum_i \int_{s_{i-1}}^{s_i} \left\{ \left[ \mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \left( \frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right) \right] + \left[ \mathbf{U}(\mathbf{q}) \frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right] \right\} ds, \quad (50)$$

where the local unit element jump boundary conditions (27a) and (27b) have been used. For the element  $m_{2(ij)}$ , where the double subscripts in parentheses indicate the corresponding element of the dyadic  $\mathbf{m}_2$ , (50) can be written as

$$\int_{V_0} R(\mathbf{q}) \frac{\partial m_{2(ij)}}{\partial t} d^3\mathbf{q} = \int_{\partial V_0} \left[ \mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \left( \frac{m_{1(i)} m_{1(j)}}{m_0} \right) - \mathbf{U}(\mathbf{q}) \left( \frac{m_{1(i)} m_{1(j)}}{m_0} \right) \right] \cdot \mathbf{n}_s ds. \quad (51)$$

Substitution of (12), (29), (45) and (48) into (51) followed by integral evaluations yields

$$\frac{dM_{2(ij)}}{dt} + \frac{dP_{2(ij)}}{dt} = \frac{W}{\bar{R}} \left[ \frac{2\bar{U}_i \bar{U}_j t}{\bar{R}} - \frac{l_j \bar{U}_i}{2} - \frac{l_i \bar{U}_j}{2} + \bar{U}_i \bar{\Phi}_j + \bar{U}_j \bar{\Phi}_i + 2\bar{D}_{ij} + \Theta_{ij} + \Theta_{ji} \right], \quad (52)$$

where

$$\Theta_{ij} = \sum_{\mathbf{b} \neq \mathbf{0}} [\nu_i^\dagger(\mathbf{b}) - j2\pi \xi_i^\dagger(\mathbf{b}) \cdot \mathbf{b}] \mu_j(\mathbf{b}), \quad (53)$$

and the dagger exponent denotes complex conjugation.

To determine the second global moment of the liquid phase solute concentration, assume a trial solution for the  $m_{2(ij)}$  entry of the dyadic  $\mathbf{m}_2$  of the form [Brenner, 1980a, b]

$$m_{2(ij)} = [E_{ij} t^2 + Z_{ij}(\mathbf{q}) t + H_{ij}(\mathbf{q})] m_0, \quad (54)$$

where  $E_{ij}$  is a constant and  $Z_{ij}(\mathbf{q})$ ,  $H_{ij}(\mathbf{q})$  are functions of the local coordinates. Evaluation of the term  $H_{ij}(\mathbf{q})$  is not necessary for the determination of the dispersion dyadic that governs the macroscopic solute transport process, because  $H_{ij}(\mathbf{q})$  has no influence on the time derivative of  $M_{2(ij)}$  (see next section). Also, combining (29) and (54) yields the second local moment of the solid phase solute concentration,

$$p_{2(ij)} = k_d(\mathbf{q}) [E_{ij} t^2 + Z_{ij}(\mathbf{q}) t + H_{ij}(\mathbf{q})] m_0. \quad (55)$$

Integrating (54) and (55) over the volume of a unit element, the trial second global moment of the liquid and solid phase solute concentrations are

$$M_{2(ij)} = (E_{ij} t^2 + \bar{Z}_{ij} t + \bar{H}_{ij}) \frac{W}{\bar{R}}, \quad (56)$$

$$P_{2(ij)} = (E_{ij} \bar{k}_d t^2 + \bar{Z}_{ij} \bar{k}_d t + \bar{H}_{ij} \bar{k}_d) \frac{W}{\bar{R}}. \quad (57)$$

Substituting (56) and (57) into (52) the constant  $E_{ij}$  is evaluated to be

$$E_{ij} = \frac{\bar{U}_i \bar{U}_j}{\bar{R}^2}. \quad (58)$$

Substituting (35) and (45) into the local unit element jump boundary condition (27a) and comparing the resulting expression to (54), it is evident that

$$Z_{ij}(\mathbf{q}) = \frac{\bar{U}_i}{\bar{R}} [\Phi_j(\mathbf{q}) - q_j] + \frac{\bar{U}_j}{\bar{R}} [\Phi_i(\mathbf{q}) - q_i] + G_{ij}, \quad (59)$$

where  $G_{ij}$  is a constant to be determined. Substitution of (58) and (59) into (54) and (55), followed by some simplifications, yields

$$G_{ij} = \frac{2\bar{D}_{ij}}{\bar{R}} + \frac{\bar{U}_i}{\bar{R}^2} \overline{[q_j - \Phi_j(\mathbf{q})]' R'(\mathbf{q})} + \frac{\bar{U}_j}{\bar{R}^2} \overline{[q_i - \Phi_i(\mathbf{q})]' R'(\mathbf{q})} + \frac{1}{\bar{R}} (\Theta_{ij} + \Theta_{ji}), \quad (60)$$

where the term  $\mathbf{F}'$  indicates the value of the function  $\mathbf{F}$  minus its average over the volume of a unit element ( $\mathbf{F}' = \mathbf{F} - \bar{\mathbf{F}}$ ), and the expression for the volume-averaged term is (see Appendix B)

$$\overline{[q_i - \Phi_i(\mathbf{q})]' R'(\mathbf{q})} = - \sum_{\mathbf{b} \neq \mathbf{0}} \lambda^\dagger(\mathbf{b}) \mu_i(\mathbf{b}). \quad (61)$$

Since all the necessary terms of the second global moment for the liquid phase solute concentration are evaluated, (56) can be written as

$$M_{2(ij)} = \left[ \frac{\bar{U}_i \bar{U}_j t^2}{\bar{R}^2} + \frac{\bar{U}_i \bar{\Phi}_j t}{\bar{R}} + \frac{\bar{U}_j \bar{\Phi}_i t}{\bar{R}} - \frac{\bar{U}_i \bar{q}_j t}{\bar{R}} - \frac{\bar{U}_j \bar{q}_i t}{\bar{R}} + \frac{2\bar{D}_{ij} t}{\bar{R}} + \frac{\Omega_{ij} t}{\bar{R}} + \bar{H}_{ij} \right] \frac{W}{\bar{R}}, \quad (62)$$

where

$$\begin{aligned} \Omega_{ij} &= \sum_{\mathbf{b} \neq \mathbf{0}} [\Psi_i^\dagger \mu_j(\mathbf{b}) + \Psi_j^\dagger \mu_i(\mathbf{b})] \\ &= 2 \sum_{\mathbf{b} \neq \mathbf{0}} \frac{(\mathbf{b} \cdot \bar{\mathbf{D}} \cdot \mathbf{b}) \operatorname{Re}(\Psi_i^\dagger \Psi_j)}{4\pi^2 (\mathbf{b} \cdot \bar{\mathbf{D}} \cdot \mathbf{b})^2 + (\bar{\mathbf{U}} \cdot \mathbf{b})^2}, \end{aligned} \quad (63)$$

$$\Psi_i = \nu_i(\mathbf{b}) - \frac{\bar{U}_i}{\bar{R}} \lambda(\mathbf{b}) - j2\pi \xi_i(\mathbf{b}) \cdot \mathbf{b}. \quad (64)$$

The latter formulation in (63) was obtained by employing (49) and the identity  $z_1^\dagger z_2 + z_2^\dagger z_1 = 2 \operatorname{Re}(z_1^\dagger z_2)$ , where  $z_1$  and  $z_2$  are complex variables and  $\operatorname{Re}$  indicates the real part of a complex variable. It should be noted that  $\Omega_{ij}$  is a function of discrete power spectra (products of Fourier coefficients).

#### EFFECTIVE COEFFICIENTS

The macroscopic velocity vector  $\mathbf{U}^\diamond$  and the macrodispersion dyadic  $\mathbf{D}^\diamond$  are defined by [Brenner, 1980a, b]

$$\mathbf{U}^\diamond = \lim_{t \rightarrow \infty} \frac{d}{dt} \left( \frac{\mathbf{M}_1}{M_0} \right), \quad (65)$$

$$\mathbf{D}^\diamond = \frac{1}{z} \lim_{t \rightarrow \infty} \frac{d}{dt} \left( \frac{\mathbf{M}_2}{M_0} - \frac{\mathbf{M}_1 \mathbf{M}_1}{M_0^2} \right). \quad (66)$$

The effective parameters governing the macroscopic solute transport under local equilibrium conditions and the prescribed flow field can now be obtained formally. In view of (37), (46) and (65) the effective velocity vector is

$$U^\diamond = \frac{1}{R} \begin{pmatrix} \bar{U}_x \\ \bar{U}_y \\ \bar{U}_z \end{pmatrix} = \frac{\bar{U}}{R} \quad (67)$$

Also, from (37), (46), (62) and (66) it follows that the macrodispersion dyadic is

$$D^\diamond = \frac{1}{R} \begin{pmatrix} D_{xx}^\diamond & D_{xy}^\diamond & D_{xz}^\diamond \\ D_{yx}^\diamond & D_{yy}^\diamond & D_{yz}^\diamond \\ D_{zx}^\diamond & D_{zy}^\diamond & D_{zz}^\diamond \end{pmatrix}, \quad (68)$$

where

$$D_{ij}^\diamond = \bar{D}_{ij} + \frac{1}{2} \Omega_{ij}. \quad (69)$$

Equation (67) indicates that the macroscopic velocity of a sorbing solute is a ratio of the volume-averaged interstitial velocity to the volume-averaged or effective retardation factor. The symmetrical macrodispersion dyadic (equation (68)), whose elements are divided by the volume-averaged retardation factor, indicates that the effective dispersion is affected by the spatial variability of the hydrogeochemical parameters considered. The enhancement of solute spreading is described by  $\Omega_{ij}/(2\bar{R})$ , where  $\Omega_{ij}$  is defined in (63). The mean hydrodynamic microdispersion coefficients may not contribute significantly to the overall macrodispersion, if the parameters  $\Omega_{ij}$  are sufficiently large ( $\Omega_{ij} \gg D_{ij}$ ). To evaluate  $\Omega_{ij}$ , knowledge of the structure of fluctuations of  $R$ ,  $U(\mathbf{q})$ , and  $D(\mathbf{q})$  is needed. It must be recognized that the expression for the macrodispersion dyadic is valid for any orientation of the mean interstitial velocity, as long as the incompressibility condition (6) holds. Moreover, for the special case of unidirectional flow in a hydraulically homogeneous porous medium,  $U(\mathbf{q}) = (\bar{U}_x, 0, 0)^T$  and  $D(\mathbf{q}) = \bar{D}$ , Equations (67)–(69) reduce to the results presented by *Chrysikopoulos et al.* [1992].

DISCUSSION

The effective macrodispersion coefficients derived (equations (67) and (68)) can be employed in the advection-dispersion equation with constant coefficients,

$$\frac{\partial \bar{C}(t, \mathbf{Q}_n)}{\partial t} = \nabla_{\mathbf{Q}_n} \cdot [D^\diamond \cdot \nabla_{\mathbf{Q}_n} \bar{C}(t, \mathbf{Q}_n)] - U^\diamond \cdot \nabla_{\mathbf{Q}_n} \bar{C}(t, \mathbf{Q}_n) \quad (70)$$

to predict the transport of  $\bar{C}(t, \mathbf{Q}_n)$  (concentration averaged over the volume of a unit element) for a sorbing solute after the plume has sampled all variations in the retardation factor and the flow field. The time period which needs to elapse before the preceding equation is applicable is known as the "relaxation time." The relaxation time can be determined as follows. The zero-order local moment, which signifies the probability that a particle occurs at certain location in the local coordinate system, is given by the time dependent solution to (74) for  $m = 0$  subject to jump boundary conditions (25a) and (25b),

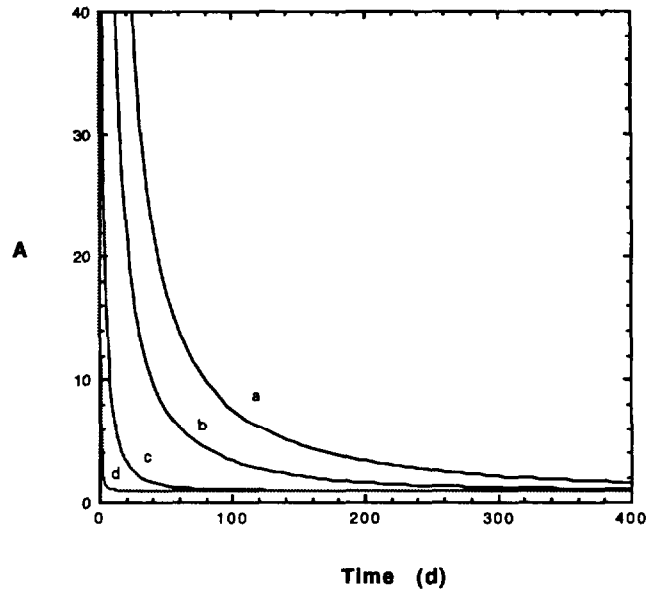


Fig. 1. The dependence of  $A$  upon time and microdispersion coefficients,  $D_{xx}/2 = D_{yy} = D_{zz}$ , of  $0.0005 \text{ m}^2/\text{d}$  (curve a),  $0.001 \text{ m}^2/\text{d}$  (curve b),  $0.005 \text{ m}^2/\text{d}$  (curve c), and  $0.05 \text{ m}^2/\text{d}$  (curve d). (Here,  $l_x/2 = l_y = l_z = 0.5 \text{ m}$ ,  $R = 10$ .)

$$m_0(t, \mathbf{q}) = \sum_{\mathbf{b}} \alpha(\mathbf{b}, t) \exp [j2\pi \mathbf{q} \cdot \mathbf{b}], \quad (71)$$

where  $\alpha(\mathbf{b}, t)$  are time dependent coefficients with absolute values given by

$$|\alpha(\mathbf{b}, t)| = |\alpha(\mathbf{b}, 0)| \exp \left[ -4\pi^2 \mathbf{b} \cdot \mathbf{D} \cdot \mathbf{b} \frac{t}{R} \right]. \quad (72)$$

The coefficients  $|\alpha(\mathbf{b}, t)|$  decay exponentially for every  $\mathbf{b} \neq \mathbf{0}$ , and

$$A(t) = \sum_{\mathbf{b}} \frac{|\alpha(\mathbf{b}, t)|}{|\alpha(\mathbf{b}, 0)|} \quad (73)$$

approaches unity at a time approximately equal to the maximum value of  $R/[4\pi^2 \mathbf{b} \cdot \mathbf{D} \cdot \mathbf{b}]$ , which corresponds to the smallest  $\mathbf{b} \neq \mathbf{0}$ , or to the lowest frequency. It should also be noted that the macroscopic coefficients indicate what values the transport parameters tend to; therefore, they are useful even if the asymptotic conditions have not yet been reached.

To illustrate the decisive role of microdispersion, local retardation and scale of periodicity in determining the time period that must elapse before the macroscopic results of this study become valid, we have plotted the variation of  $A$  with time for a variety of conditions. For presentation purposes, the curves appearing in Figures 1–4 are obtained for the special case where  $D_{xx}/2 = D_{yy} = D_{zz}$  and  $l_x/2 = l_y = l_z$ . The range of the transport parameters used in the figures is chosen to encompass most of the commonly encountered subsurface conditions.

Figure 1 illustrates the dependence of  $A$  upon time for several sets of microdispersion coefficients. As the microdispersion coefficients get larger,  $A(t)$  declines exponentially to its asymptotic value at a faster rate. Note that  $m_0$  becomes constant as soon as  $A(t)$  approaches unity. For the

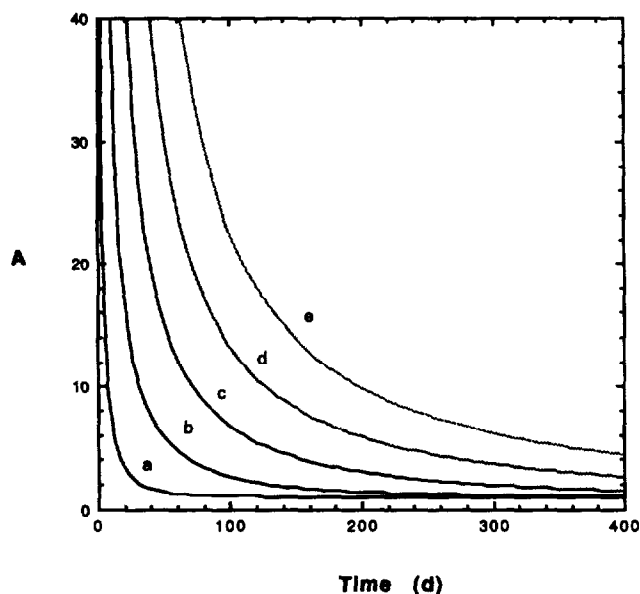


Fig. 2. The dependence of  $A$  upon time and scales of periodicity,  $l_x/2 = l_y = l_z$ , of 0.5 m (curve a), 1.0 m (curve b), 1.5 m (curve c), 2.0 m (curve d), and 2.5 m (curve e). ( $D_{xx}/2 = D_{yy} = D_{zz} = 0.005 \text{ m}^2/\text{d}$ ,  $R = 10$ .)

transport conditions considered in this exercise, a tenfold increase in the microdispersion coefficients reduces the relaxation time by approximately a factor of 10 (i.e., compare curves *c* and *d*), indicating that the relaxation time is inversely proportional to microdispersion coefficients. The dependence of  $A$  upon time and scale of periodicity is shown in Figure 2. A twofold increase in  $l_i$  increases the relaxation time by a factor of 4 (i.e., compare curves *a* and *b*). Clearly, the relaxation time is proportional to the square of the periodicity scale. Figure 3 illustrates the linear relationship between the relaxation time and the retardation factor. Therefore, a rough estimate of the time required for  $A(t)$  to

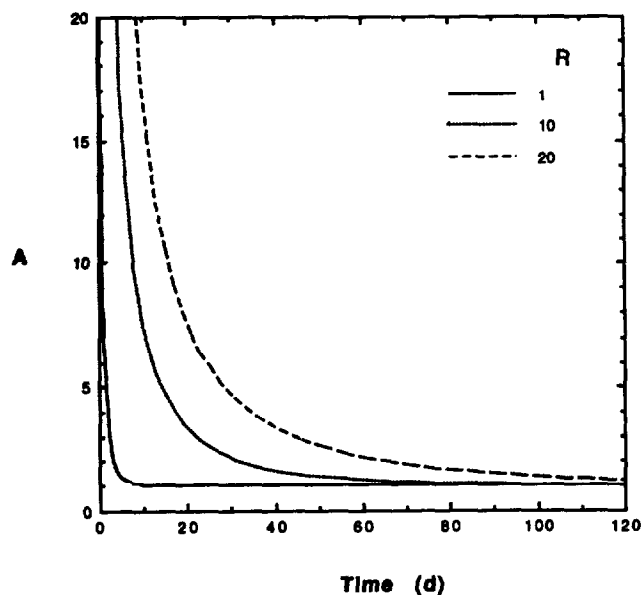


Fig. 3. The dependence of  $A$  upon time and retardation factor ( $D_{xx}/2 = D_{yy} = D_{zz} = 0.005 \text{ m}^2/\text{d}$ ,  $l_x/2 = l_y = l_z = 0.5 \text{ m}$ ).

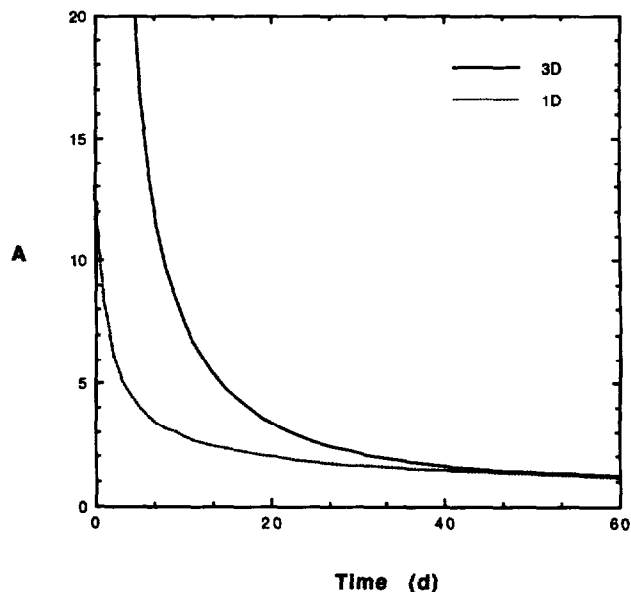


Fig. 4. The dependence of  $A$  upon time for one- and three-dimensional sorbing solute transport.

approach unity, or equivalently a very rough estimate of the relaxation time, is  $l^2 \hat{R}/\hat{D}$ , where  $\hat{R}$ ,  $\hat{D}$  are typical values of the retardation factor and the microdispersion coefficient, respectively, and  $l$  is the scale of periodicity. Similar expressions of the relaxation time, for different but related problems, have been derived by Dagan [1982b] and Kitanidis [1990]. Although macrodispersion is not crucially affected by microdispersion variations [Vomvoris, 1986; Dagan, 1987], the pore-scale dispersivity, together with the local retardation factor and the scale of periodicity, controls the relaxation time and consequently determines when the macrodispersion theory is applicable.

The relaxation time for organic solutes in groundwater formations under natural gradient conditions may be quite long. For example, consider the halogenated organic solute 1,2-dichlorobenzene (DCB) which was used during the long-term solute transport experiment at Canadian Forces Base, Borden, Ontario [Mackay et al., 1986b]. Among the five organic solutes investigated at the Borden site, DCB is the second most strongly retarded compound with retardation factor equal to 3.9, as estimated from synoptic sampling after a 15-day time period [Roberts et al., 1986]. The correlation scales of the natural log of hydraulic conductivity of the aquifer in directions parallel and transverse to the mean interstitial velocity vector are 5.14 and 8.33 m, respectively, whereas the vertical correlation scale is in the range 0.21–0.34 m [Woodbury and Sudicky, 1991]. Since the spatial variability of DCB sorption and the microdispersion coefficients of the aquifer are presently not available in the literature, we assume that the correlation scales of sorption are smaller than the correlation scales of the hydraulic conductivity,  $D_{xx} = 0.005$ ,  $D_{yy} = D_{zz} = 0.0005 \text{ m}^2/\text{d}$ , and that the scales of periodicity are approximately equal to the correlation scales of hydraulic conductivity. For this set of hydrogeochemical parameters and assumptions the relaxation time for DCB in the Borden site is over 110 years. Furthermore, for the case where  $\alpha(\eta) = \bar{\alpha} = 1$  (conservative tracer) the relaxation time is approximately 28 years.



The last sampling session at the Borden aquifer was 1038 days after injection [Mackay *et al.*, 1986b]; therefore, according to this analysis, the injected solutes may not have reached asymptotic conditions. The spatial moments of the data, analyzed by Freyberg [1986], show that asymptotic conditions had not been reached by the end of the experiment. Certainly, it is hard to use the relaxation time to pinpoint the time the Borden plume(s) are reaching the asymptotic domain because (1) the plume is already spread out at time  $t = 0$  (distributed injection); and (2) the appropriate characteristic lengths ("periods") are probably multiples of the correlation lengths but their exact size is unspecified if the medium is not periodic.

The relaxation time for one- and three-dimensional porous formations may not be equal. For example, in Figure 4, we have compared the dependence of  $A(t)$  upon time for one- and three-dimensional porous media. Clearly, asymptotic conditions are reached faster in the one-dimensional system. This result is intuitively expected, because in a one-dimensional porous medium the solute samples only the parameter fluctuations in the longitudinal direction, whereas in a three-dimensional porous medium the solute must sample parameter variabilities in all three directions. Since the relaxation time is inversely proportional to microdispersion coefficients, the large relaxation time shown for the three-dimensional case is attributable to the coefficients  $D_{yy}$  and  $D_{zz}$ , which are smaller than  $D_{xx}$ .

The Taylor-Aris-Brenner method of moments makes use of spatial averaging of the aqueous solute concentration,  $C$ , as opposed to  $RC$  which corresponds to the total concentration (aqueous plus sorbed solute mass). For example, the large-time or effective velocity  $\bar{U}/\bar{R}$  of a solute sorbing under local equilibrium conditions represents the aqueous solute velocity in a heterogeneous porous medium with periodic hydrogeochemical parameters. The same expression for the effective velocity was found by Dagan [1989], Valocchi [1989] and Chrysikopoulos *et al.* [1992]. However, Kabala and Sposito [1991] suggested that the field-scale velocity is given by  $\bar{U}/\bar{R}$ . This result is valid when the total concentration is uniformly distributed within the porous medium, a situation which can be encountered at early times of an injection experiment with a uniform flux- or third-type upstream boundary condition.

The method of moments employed in this work for the determination of macroscopic parameters makes use of spatial averaging in a single formation with periodic hydrogeochemical parameters. It thus is an alternative to the stochastic approach which employs averaging over the ensemble of all realizations of a stationary random field. The relation between the two approaches has been explored through comparison in special cases and, interestingly enough, it has been found that the two approaches yield essentially the same large-time results. It has been shown in the head covariance [Van Lent and Kitanidis, 1989] and effective conductivity cases [Kitanidis, 1990] that the result of the stochastic model can be approximated at any degree of accuracy by sufficiently increasing the period in the periodic model.

The assumption that retardation is governed by a linear equilibrium isotherm under nearly ideal, local chemical equilibrium conditions is by no means applicable to every hydrogeological setting. However, this study is focused on the fundamentals of sorbing solute macrodispersion in heterogeneous porous formations, and the local equilibrium

assumption is just a starting point for generalization to more complicated systems. In relatively complex field sites the transport of organic solutes under natural gradient conditions might be affected by nonlinear equilibrium sorption behavior, hysteresis, biotransformation, and slow approach to sorption equilibrium [Roberts *et al.*, 1986; Curtis *et al.*, 1986]. Deviations from local equilibrium may lead to considerably different effective macrodispersion coefficients. For example, in the special cases examined by Valocchi [1989] and Chrysikopoulos *et al.* [1992], it was shown that the longitudinal macrodispersion coefficient is greater for first-order kinetic sorption than linear equilibrium sorption.

#### SUMMARY

Taylor-Aris-Brenner moment analysis was employed to derive the effective velocity vector and macrodispersion dyadic for sorbing solute transport under local equilibrium conditions in a three-dimensional porous medium with spatially periodic interstitial velocity field, microdispersion coefficients and retardation factor in all three directions. The periodic parameters were assumed to possess identical spatial periods in each principal direction of a Cartesian coordinate system. The domain is divided into rectangular parallelepipeds or unit elements with identical properties. It was shown that the field-scale effective solute velocity for the aqueous concentration is the volume-averaged interstitial velocity over the volume-averaged retardation factor, and the effective dispersion is the volume-averaged microdispersion over the volume-averaged retardation factor plus a term expressing the increase in solute spreading from the spatial variability of the hydrogeochemical parameters. A perturbation or first-order method was employed for the derivation of the expressions presented; thus, the results are valid only for the case where the spatially periodic parameters have "small" fluctuations. The range of applicability of the results remains to be explored. The results derived in this work are valid for any orientation of the mean velocity, assuming that the steady state interstitial fluid velocity is nondivergent. The effective macrodispersion coefficients (equations (67) and (68)) can be employed in the advection-dispersion equation with constant effective coefficients to predict the transport of volume-averaged concentration for a sorbing solute after the plume has sampled all variations in the retardation factor and the flow field. The macroscopic coefficients are useful even if the asymptotic conditions have not yet been reached, because they show us what values the transport parameters tend to. It was shown that the pore-scale dispersivity, the local retardation factor, and the scale of periodicity are crucially important in determining the time period needed for the effective velocity and the effective macrodispersion coefficient to become constant.

#### APPENDIX A: DERIVATION OF $\mu_x(\mathbf{q})$

Substituting (45) (for  $i = x$ ) into (24), (26a), and (26b) leads to the following set of partial differential equation and local jump conditions:

$$R(\mathbf{q}) \frac{\bar{U}_x}{\bar{R}} - U_x(\mathbf{q}) = \nabla_{\mathbf{q}} \cdot [\mathbf{D}(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \Phi_x(\mathbf{q})] - \nabla_{\mathbf{q}} \cdot \mathbf{d}_x(\mathbf{q}) - U(\mathbf{q}) \cdot \nabla_{\mathbf{q}} \Phi_x(\mathbf{q}), \quad (\text{A1})$$

$$[\Phi_x(\mathbf{q})] = 0, \quad (\text{A2a})$$

$$[\nabla_{\mathbf{q}}\Phi_x(\mathbf{q})] = 0, \quad (\text{A2b})$$

where  $\mathbf{d}_x(\mathbf{q}) = (D_{xx}, D_{yx}, D_{zx})^T$  is the first column of the microdispersion coefficient tensor. Since  $R(\mathbf{q})$ ,  $\mathbf{U}(\mathbf{q})$ , and  $\mathbf{D}(\mathbf{q})$  are periodic in all three directions, they can be expanded into the following Fourier series:

$$R(\mathbf{q}) = \bar{R} + R'(\mathbf{q}) = \bar{R} + \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \lambda(\mathbf{b}) \exp [j2\pi\mathbf{q} \cdot \mathbf{b}], \quad (\text{A3})$$

$$\mathbf{U}(\mathbf{q}) = \bar{\mathbf{U}} + \mathbf{U}'(\mathbf{q}) = \bar{\mathbf{U}} + \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \nu(\mathbf{b}) \exp [j2\pi\mathbf{q} \cdot \mathbf{b}], \quad (\text{A4})$$

$$\mathbf{D}(\mathbf{q}) = \bar{\mathbf{D}} + \mathbf{D}'(\mathbf{q}) = \bar{\mathbf{D}} + \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \xi(\mathbf{b}) \exp [j2\pi\mathbf{q} \cdot \mathbf{b}], \quad (\text{A5})$$

where  $\lambda(\mathbf{b})$  is a scalar,  $\nu(\mathbf{b})$  is a vector, and  $\xi(\mathbf{b})$  is a symmetric matrix of known coefficients, given by

$$\lambda(\mathbf{b}) = \frac{1}{V_0} \int_{V_0} R(\mathbf{q}) \exp [-j2\pi\mathbf{q} \cdot \mathbf{b}] d^3\mathbf{q}, \quad (\text{A6})$$

$$\nu(\mathbf{b}) = \frac{1}{V_0} \int_{V_0} \mathbf{U}(\mathbf{q}) \exp [-j2\pi\mathbf{q} \cdot \mathbf{b}] d^3\mathbf{q}, \quad (\text{A7})$$

$$\xi(\mathbf{b}) = \frac{1}{V_0} \int_{V_0} \mathbf{D}(\mathbf{q}) \exp [-j2\pi\mathbf{q} \cdot \mathbf{b}] d^3\mathbf{q}. \quad (\text{A8})$$

Note that  $\lambda(\mathbf{b}) = \lambda^\dagger(-\mathbf{b})$ ,  $\nu(\mathbf{b}) = \nu^\dagger(-\mathbf{b})$ , and  $\xi(\mathbf{b}) = \xi^\dagger(-\mathbf{b})$ . Substituting (A3)–(A5) and (48) into the governing equation (A1) leads to

$$\begin{aligned} & (\varepsilon^0 \bar{R} + \varepsilon^1 R'(\mathbf{q})) \frac{\varepsilon^0 \bar{U}_x}{\varepsilon^0 \bar{R}} - (\varepsilon^0 \bar{U}_x + \varepsilon^1 U'_x(\mathbf{q})) \\ & = \nabla_{\mathbf{q}} \cdot [(\varepsilon^0 \bar{\mathbf{D}} + \varepsilon^1 \mathbf{D}'(\mathbf{q})) \cdot \nabla_{\mathbf{q}} (\varepsilon^0 \bar{\Phi}_x + \varepsilon^1 \Phi'_x(\mathbf{q}))] \\ & \quad - \nabla_{\mathbf{q}} \cdot (\varepsilon^0 \bar{\mathbf{d}}_x + \varepsilon^1 \mathbf{d}'_x(\mathbf{q})) - (\varepsilon^0 \bar{\mathbf{U}} + \varepsilon^1 \mathbf{U}'(\mathbf{q})) \\ & \quad \cdot \nabla_{\mathbf{q}} (\varepsilon^0 \bar{\Phi}_x + \varepsilon^1 \Phi'_x(\mathbf{q})), \end{aligned} \quad (\text{A9})$$

where the superscript 0 indicates zero-order terms, and the superscript 1 designates first-order terms. Note that the introduction of  $\varepsilon$  is solely a mathematical artifice which permits separation of the "small" high-order terms from the larger low-order terms, and bookkeeping of terms of the same order. The preceding equation must be satisfied separately for terms of each order. Equating coefficients of  $\varepsilon^0$  in (A9) yields

$$\nabla_{\mathbf{q}} \cdot (\bar{\mathbf{D}} \cdot \nabla_{\mathbf{q}} \bar{\Phi}_x) - \bar{\mathbf{U}} \cdot \nabla_{\mathbf{q}} \bar{\Phi}_x = 0. \quad (\text{A10})$$

By inspection we can deduce that the preceding equation is satisfied since  $\bar{\Phi}_x$  is a constant. Equating coefficients of  $\varepsilon^1$  in (A9) yields

$$\begin{aligned} R'(\mathbf{q}) \frac{\bar{U}_x}{\bar{R}} - U'_x(\mathbf{q}) \\ = \nabla_{\mathbf{q}} \cdot [\mathbf{D} \cdot \nabla_{\mathbf{q}} \Phi'_x(\mathbf{q})] - \nabla_{\mathbf{q}} \cdot \mathbf{d}'_x(\mathbf{q}) - \mathbf{U} \cdot \nabla_{\mathbf{q}} \Phi'_x(\mathbf{q}). \end{aligned} \quad (\text{A11})$$

Employing the Fourier expansions of  $R'$ ,  $U'_x$ ,  $\mathbf{d}'_x$ , and  $\Phi'_x$  in (A11) yields

$$\sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \left\{ \frac{\bar{U}_x}{\bar{R}} \lambda(\mathbf{b}) - \nu_x(\mathbf{b}) + (4\pi^2 \mathbf{b} \cdot \bar{\mathbf{D}} \cdot \mathbf{b} + j2\pi \bar{\mathbf{U}} \cdot \mathbf{b}) \mu_x(\mathbf{b}) + j2\pi \xi_x(\mathbf{b}) \cdot \mathbf{b} \right\} \exp [j2\pi\mathbf{q} \cdot \mathbf{b}] = 0, \quad (\text{A12})$$

where  $\nu_x(\mathbf{b})$  is the first element of the coefficient vector  $\nu(\mathbf{b})$ , and  $\xi_x(\mathbf{b})$  is the first column of the coefficient matrix  $\xi(\mathbf{b})$ . Since the complex exponentials form a complete orthogonal basis, the bracketed expression in the previous equation must be zero for every  $\mathbf{b} \neq \mathbf{0}$ . Hence, it follows that

$$\mu_x(\mathbf{b}) = \frac{\nu_x(\mathbf{b}) - (\bar{U}_x/\bar{R})\lambda(\mathbf{b}) - j2\pi \xi_x(\mathbf{b}) \cdot \mathbf{b}}{4\pi^2 \mathbf{b} \cdot \bar{\mathbf{D}} \cdot \mathbf{b} + j2\pi \bar{\mathbf{U}} \cdot \mathbf{b}} \quad (\text{A13})$$

$(\mathbf{b} \neq \mathbf{0}),$

In a similar fashion the expressions for  $\mu_y(\mathbf{q})$  and  $\mu_z(\mathbf{q})$  are derived.

#### APPENDIX B: DERIVATION OF $\overline{[q_i - \Phi_i(\mathbf{q})]'R'(\mathbf{q})}$

In this appendix the expression for the volume-averaged term that appears in the effective global dispersion coefficients is developed. By definition

$$\overline{[q_i - \Phi_i(\mathbf{q})]'R'(\mathbf{q})} \stackrel{\text{def}}{=} \frac{1}{V_0} \int_{V_0} [q_i - \Phi_i(\mathbf{q})]'R'(\mathbf{q}) d^3\mathbf{q}, \quad (\text{B1})$$

where

$$q'_i = q_i - l_i/2, \quad (\text{B2})$$

$$R'(\mathbf{q}) = \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \lambda(\mathbf{b}) \exp [j2\pi\mathbf{q} \cdot \mathbf{b}], \quad (\text{B3})$$

$$\Phi'(\mathbf{q}) = \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \mu(\mathbf{b}) \exp [j2\pi\mathbf{q} \cdot \mathbf{b}]. \quad (\text{B4})$$

Combining equations (B1)–(B4) and assuming that integrations and summations are interchangeable leads to

$$\begin{aligned} & \overline{[q_i - \Phi_i(\mathbf{q})]'R'(\mathbf{q})} \\ & = \frac{1}{V_0} \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \lambda(\mathbf{b}) \int_{V_0} (q_i - l_i/2) \exp [j2\pi\mathbf{q} \cdot \mathbf{b}] d^3\mathbf{q} \\ & \quad - \frac{1}{V_0} \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \sum_{\substack{\mathbf{k} \\ \mathbf{k} \neq \mathbf{0}}} \lambda(\mathbf{k}) \mu(\mathbf{b}) \int_{V_0} \exp [j2\pi\mathbf{q} \cdot (\mathbf{k} + \mathbf{b})] d^3\mathbf{q} \\ & = - \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \lambda(-\mathbf{b}) \mu(\mathbf{b}), \end{aligned} \quad (\text{B5})$$

where the following equation has been employed:

$$\frac{1}{V_0} \int_{V_0} \exp [j2\pi \mathbf{q} \cdot (\hat{\mathbf{b}} + \hat{\mathbf{k}})] d^3 \mathbf{q} = 1 \quad \mathbf{b} = -\mathbf{k}; \tag{B6}$$

$$\frac{1}{V_0} \int_{V_0} \exp [j2\pi \mathbf{q} \cdot (\hat{\mathbf{b}} + \hat{\mathbf{k}})] d^3 \mathbf{q} = 0 \quad \mathbf{b} \neq -\mathbf{k}.$$

Since  $\lambda(-\mathbf{b}) = \lambda^+(\mathbf{b})$ , (B5) becomes

$$\overline{[q_i - \Phi_i(\mathbf{q})]' R'(\mathbf{q})} = - \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq \mathbf{0}}} \lambda^+(\mathbf{b}) \mu(\mathbf{b}). \tag{B7}$$

NOTATION

- A** defined in (73).
- b** vector of integers (wavenumbers), equal to  $(b_x, b_y, b_z)^T$ .
- b̂** normalized vector, equal to  $(b_x/l_x, b_y/l_y, b_z/l_z)^T$ .
- ℘** denotes **R**, **U**, **D**.
- C** liquid phase solute concentration (solute mass/liquid volume),  $M/L^3$ .
- C\*** solid phase or sorbed solute concentration (solute mass/solid mass),  $M/M$ .
- d<sub>i</sub>** column of the microdispersion coefficient tensor i.e.,  $\mathbf{d}_y = (D_{xy}, D_{yy}, D_{zy})^T$ .
- D<sub>ij</sub>** hydrodynamic microdispersion coefficient,  $L^2/t$ .
- D** microdispersion coefficient tensor.
- E<sub>ij</sub>** constant.
- F** arbitrary global or local function.
- G<sub>ij</sub>** constant.
- H<sub>ij</sub>** function of local coordinates.
- j** imaginary number unit equal to  $\sqrt{-1}$ .
- k<sub>d</sub>** dimensionless partition or distribution coefficient.
- k** vector of integers (wavenumbers), equal to  $(k_x, k_y, k_z)^T$ .
- k̂** normalized vector, equal to  $(k_x/l_x, k_y/l_y, k_z/l_z)^T$ .
- K<sub>d</sub>** partition or distribution coefficient (liquid volume/solid mass),  $L^3/M$ .
- l<sub>i</sub>** characteristic linear dimension of a unit element,  $L$ .
- l<sub>i</sub>** basic vectors which define a unit element.
- m<sub>m</sub>** liquid phase moments.
- M<sub>m</sub>** continuous and discrete representation of liquid phase global moments.
- n<sub>s</sub>** outer unit vector normal to  $\partial V_0$ .
- O** order of magnitude.
- p<sub>m</sub>** solid phase local moments.
- P<sub>m</sub>** continuous and discrete representation of solid phase global moments.
- q<sub>i</sub>** local Cartesian coordinates,  $L$ .
- q** local position vector within a unit element.
- ∂q<sub>i</sub>** interface of a unit element.
- d<sup>3</sup>q** differential volume within a unit element.
- Q<sub>i</sub>** global Cartesian coordinates,  $L$ .
- Q** discrete position vector of a general point.
- Q<sub>n</sub>** discrete position vector locating the origin of the *n*th unit element.
- R** retardation factor.

- Re** real.
- s<sub>±i</sub>** faces of the unit element.
- ds** infinitesimal area on  $\partial V_0$ .
- S\*** solid phase or sorbed solute concentration (solute mass/liquid volume),  $M/L^3$ .
- t** time,  $t$ .
- U<sub>i</sub>** interstitial velocity,  $L/t$ .
- U** velocity vector.
- V<sub>0</sub>** domain of a unit element, equal to  $l_x l_y l_z$ .
- ∂V<sub>0</sub>** external surface of a unit element.
- W** mass of solute injected,  $M$ .
- Z<sub>ij</sub>** function of local coordinates.
- Γ<sub>i</sub>** constant.
- δ( )** Dirac delta function.
- δ<sub>ij</sub>** Kronecker delta.
- ε** mathematical artifice, scalar.
- θ** porosity (liquid volume/aquifer volume),  $L^3/L^3$ .
- Θ<sub>ij</sub>** defined in (53).
- λ, μ, ν, ξ** Fourier coefficients.
- ρ** bulk density of the solid matrix (solid mass/aquifer volume),  $M/L^3$ .
- Σ** summation.
- Φ** function of local coordinates.
- Ψ<sub>ij</sub>** defined in (64).
- Ω<sub>ij</sub>** defined in (63).
- 0** null vector.
- ∈** an element of.
- ∇<sub>q</sub>** vector operator (del), equal to  $[\partial/\partial q_x, \partial/\partial q_y, \partial/\partial q_z]^T$ .
- ≡<sup>def</sup>** equals by definition.
- |** given that.
- ||** magnitude of a vector; Euclidean norm.
- ||** jump in the value of a function across equivalent points on opposite faces of a unit element.

Subscripts

- i, j, k** direction of principal axes, equal to  $x, y, z$ .
- n** *n*th unit element:  $\{\mathbf{n}\} = \{n_x, n_y, n_z\}$ .
- x, y, z** principal directions of a Cartesian coordinate system.

Superscripts

- T** transpose.
- \*** solid phase.
- ◇** macroscopic coefficient.
- '** value of a function minus its average over the volume of a unit element.
- +** complex conjugate.

An overdot denotes average over the volume of a unit element.

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- C. V. Chrysikopoulos, Department of Civil Engineering, University of California, Irvine, CA 92717.  
P. K. Kitanidis and P. V. Roberts, Department of Civil Engineering, Stanford University, Stanford, CA 94305.

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