Generalized TaylorAris moment analysis of the transport of sorbing solutes through porous media with spatiallyperiodic retardation factor. Transp Porous Media 7:163–185

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Generalized Taylor–Aris Moment Analysis of the Transport of Sorbing Solutes Through Porous Media with Spatially–Periodic Retardation Factor

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Abstract. Taylor–Aris dispersion theory, as generalized by Brenner, is employed to investigate the macroscopic behavior of sorbing solute transport in a three-dimensional, hydraulically homogeneous porous medium under steady, unidirectional flow. The porous medium is considered to possess spatially periodic geochemical characteristics in all three directions, where the spatial periods define a rectangular parallelepiped or a unit-element. The spatially-variable geochemical parameters of the solid matrix are incorporated into the transport equation by a spatially-periodic distribution coefficient and consequently a spatially-periodic retardation factor. Expressions for the effective or large-time coefficients governing the macroscopic solute transport are derived for solute sorbing according to a linear equilibrium isotherm as well as for the case of a first-order kinetic sorption relationship. The results indicate that for the case of a chemical equilibrium sorption isotherm the longitudinal macrodispersion incorporates a second term that accounts for the effect of averaging the distribution coefficient over the volume of a unit element. Furthermore, for the case of a kinetic sorption relation, the longitudinal macrodispersion expression includes a third term that accounts for the effect of the first-order sorption rate. Therefore, increased solute spreading is expected if the local chemical equilibrium assumption is not valid. The derived expressions of the apparent parameters governing the macroscopic solute transport under local equilibrium conditions agreed reasonably with the results of numerical computations using particle tracking techniques.

Key words. Moment analysis, sorbing solute transport, spatially-periodic retardation.

1. Nomenclature

A	amplitude of oscillation of the retardation factor
$\mathbf{b}$	vector of wavenumbers: $\mathbf{b} = (b_x, b_y, b_z)^T$
$\check{\mathbf{b}}$	normalized vector: $\check{\mathbf{b}} = (b_x/l_x, b_y/l_y, b_z/l_z)^T$
C	liquid-phase solute concentration (solute mass/liquid volume), M/L^3
C^*	solid-phase or sorbed solute concentration (solute mass/solids mass), M/M
$\check{C}_n$	total liquid-phase solute mass within the nth unit element, M
D_{ij}	hydrodynamic dispersion coefficient, L^2/t
$\mathbf{D}$	dispersion coefficient tensor
E_{ij}	constant
F	arbitrary global or local function
H_{ij}	function of local coordinates

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j imaginary number unit: $j = \sqrt{-1}$

k_d, k_d^0 dimensionless partition or distribution coefficients

k_f forward sorption rate coefficient, t^{-1}

k_r reverse sorption rate coefficient, t^{-1}

K_d partition of distribution coefficient (liquid volume/solids mass), L^3/M

l_i characteristic linear dimension of a unit element, L

$\mathbf{l}_i$ basic vectors which define a unit element

$\mathbf{m}_m$ liquid-phase local moments

$\mathbf{M}_m$ continuous and discrete representation of liquid-phase global moments

$\mathbf{n}_s$ outer unit vector normal to ∂V_o

o origin of a local coordinate system

O order of magnitude, origin of global coordinate system

$\mathbf{p}_m$ solid-phase local moments

$\mathbf{P}_m$ continuous and discrete representation of solid-phase global moments

q_i local Cartesian coordinates, L

$\mathbf{q}$ local position vector within a unit element

$\partial \mathbf{q}_i$ interface of a unit element

$d^3\mathbf{q}$ differential volume within a unit element

Q_i global Cartesian coordinates, L

$\mathbf{Q}$ discrete position vector of a general point

$\mathbf{Q}_n$ discrete position vector locating the origin of the nth unit element

R, R^0 retardation factors defined in Equations (8) and (85), respectively

$s_{\pm i}$ faces of the unit element

ds infinitesimal area on ∂V_o

S^* solid-phase or sorbed solute concentration (solute mass/liquid volume), M/L^3

$\check{S}_n^*$ total solid-phase solute mass within the n unit element

t time, t

U average interstitial velocity, L/t

$\mathbf{U}$ velocity vector

V_o domain of a unit element

∂V_o external surface of a unit element

W mass of solute injected, M

Z_{ij} function of local coordinates

Γ constant

$\delta(\ )$ Dirac delta function

δ_{ij} Kronecker delta

θ porosity (liquid volume/aquifer volume), L^3/L^3

λ spectrum coefficient

μ spectrum coefficients, L

ρ bulk density of the solid matrix (solids mass/aquifer volume), M/L^3

Σ summation

Φ function of local coordinates

0   null vector

$\in$ an element of

∇_q vector operator (del): $\nabla_q = [\partial/\partial q_x, \partial/\partial q_y, \partial/\partial q_z]^T$

$\overset{\text{def}}{=}$ equals by definition

$\forall$ for all

$|\ |$ 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 direction of principal axes: $i, j = x, y, z$

m, n integer summation indicies

n nth unit element: $\{n\} = \{n_x, n_y, n_z\}$

x, y, z principal directions of a Cartesian coordinate system

Superscripts

T transpose

$*$ indicates the solid-phase

$\diamond$ effective global coefficient

$\triangleleft$ indicates the value of a function minus its average over the volume of a unit element

$\dagger$ complex conjugate

$\bullet$ local equilibrium sorption

$\bullet\bullet$ first-order reversible kinetic sorption

$-$ (overbar) average over the volume of a unit element

2. Introduction

Recent solute transport laboratory studies (Durant and Roberts, 1986) and a field experiment (Mackay *et al.*, 1986; Roberts *et al.*, 1986) indicate that in modeling sorbing solute transport through natural subsurface systems the retardation factor should not be considered as a position-independent constant, but rather as a spatially-variable parameter. The problem of how to model the impact of spatially-variable retardation on the transport and spreading of sorbing solutes through porous media is increasingly capturing the attention of investigators from various disciplines. Garabedian (1987) assumed that the log-hydraulic conductivity is linearly related to the porosity and the distribution coefficient, and employed spectral small-perturbation techniques to show that a negative correlation between the log-hydraulic conductivity and the distribution coefficient increases ensemble solute dispersion. Similar results were obtained by Valocchi (1989), who used the method moments to study the asymptotic behavior of sorbing solute transport in perfectly stratified porous media and two-layer aquifers under the assumption that pore water velocity, dispersion coefficients, distribution coefficients and sorption rate coefficients are vertically-distributed. Dagan (1989, p. 344) assumed a linear

correlation between log-hydraulic conductivity and retardation factor to derive some preliminary results for the average velocity and macrodispersion coefficients of a particle displacement. Van der Zee and van Riemsdijk (1987) employed the parallel-column model to derive an expression for the field-averaged profile of solid-phase solute concentration, assuming that each homogeneous column differs with respect to the fluid velocity, retardation factor, and time period of solute input, all of which are treated as lognormally distributed. Chrysikopoulos *et al.* (1990) derived an analytical small-perturbation solution to the partial diffierential equation describing one-dimensional sorbing solute transport through homogeneous porous media with spatially-variable retardation factor.

The majority of the mathematical models currently used to simulate transport of solutes undergoing sorption or ion exchange assume local equilibrium, neglecting rate limitations in the interest of computational simplicity. However, the validity of the local equilibrium assumption has been questioned repeatedly in studies of sorbing solute transport through laboratory column (James and Rubin, 1979; Nkedi-Kizza *et al.*, 1983; Miller and Weber, 1986) and in field (Pickens *et al.*, 1981; Goltz and Roberts, 1986; Roberts *et al.*, 1986; Knapp, 1989) systems. In attempting to identify conditions for which the assumption of local chemical equilibrium is applicable, a variety of techniques have been developed. Valocchi (1985) applied the method of mements to obtain criteria for the use of equilibrium models, Parker and Valoochi (1986) derived conditions for quantitative evaluation of the equivalence between equilibrium and first-order kinetic solute transport models. Bahr and Rubin (1987) also presented a procedure for direct comparison between simple equilibrium and kinetic transport models. Furthermore, studies in solute transport have expanded to account for the important case where multiple species are transported simultaneously and interact. Such complex multicomponent transport models usually are formulated either by incorporating the chemical reaction equations directly into the governing transport equation (Valocchi *et al.*, 1981; Jennings *et al.*, 1982; Miller and Benson, 1983; Kirkner *et al.*, 1984; Angelakis *et al.*, 1987; Mansell *et al.*, 1988) or by separating the equations describing the chemical interactions and solute transport (Cederberg *et al.*, 1985; Liu and Narasimhan, 1989).

The present work focuses on the transport of sorbing but otherwise nonreacting solutes under either local equilibrium or first-order kinetically sorbing conditions in a three-dimensional hydraulically homogeneous but geochemically spatially-periodic porous medium. Geochemical periodicity refers to the case where the distribution coefficient, and consequently the retardation factor, repeat themselves with a certain period in each direction. Generalized Taylor–Aris dispersion theory is employed to derive expressions for the apparent or asymptotic coefficients, namely the mean velocity vector and dispersion dyadic, governing the macroscopic solute transport process. Despite the fact that a three-dimensional porous medium is considered, the present analysis is limited to unidirectional flow, but can be extended to the more general cases of two- or three-dimensional flow fields

(Chrysikopoulos *et al.*, 1991). The assumption of a geochemically spatially-periodic porous medium may be criticized, because the geochemical characteristics of field formations although recurrent in space are not exactly periodic. It has been employed for mathematical convenience because it leads to exact expressions. The periodic model is the simplest way to represent spatial repetitiveness and can be used as an intermediate step to obtain results for the more general stationary case, as illustrated by Kitanidis (1990) for the hydraulic conductivity case.

3. Problem Formulation

Consider a three-dimensional porous medium with spatially-periodic geochemical parameters in all three directions. Assuming that the variability in each principal direction of a Cartesian coordinate system has spatial period l_x, l_y, and l_z, respectively, the porous medium may be divided into identical rectangular parallelepiped elements with edges defined by the vectors $\mathbf{1}_x$, $\mathbf{1}_y$, and $\mathbf{1}_z$ (e.g., $\mathbf{1}_y = (0, l_y, 0)^T$). A vector of spatial coordinates $\mathbf{Q}$ may be written as the sum of an unbounded *global* variable $\mathbf{Q}_n$ and a bounded *local* variable q (Brenner, 1980b; Brenner and Adler, 1982). Explicitly,

$$\mathbf{Q} = \mathbf{Q}_n + \mathbf{q}, \tag{1}$$

where

$$\mathbf{Q}_n = \begin{pmatrix} n_x l_x \\ n_y l_y \\ n_z l_z \end{pmatrix}; \qquad \mathbf{q} = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix}, \tag{2a,b}$$

$$n_i = 0, \pm 1, \pm 2, \pm 3, \ldots, \quad (i = x, y, z), \tag{3a}$$

$$0 \leqslant q_x \leqslant l_x$$

$$0 \leqslant q_y \leqslant l_y \tag{3b}$$

$$0 \leqslant q_z \leqslant l_z$$

and the subscript **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 (see Figure 1).

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

$$\frac{\partial C(t, \mathbf{Q})}{\partial t} + \frac{\rho}{\theta} \frac{\partial C^*(t, \mathbf{Q})}{\partial t} = D_{xx} \frac{\partial^2 C(t, \mathbf{Q})}{\partial Q_x^2} + D_{yy} \frac{\partial^2 C(t, \mathbf{Q})}{\partial Q_y^2}$$

$$+ D_{zz} \frac{\partial^2 C(t, \mathbf{Q})}{\partial Q_z^2} - U_x \frac{\partial C(t, \mathbf{Q})}{\partial Q_x}, \tag{4}$$

where $C(t, \mathbf{Q})$, which can also be written as $C(t, \mathbf{Q}_n, \mathbf{q})$, is the volume-averaged or
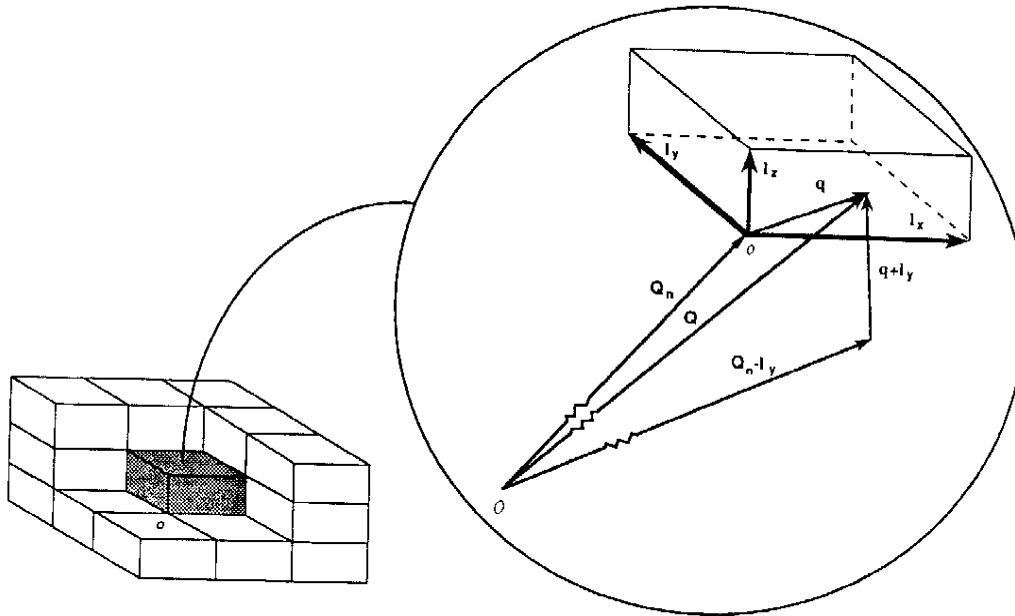
Fig. 1. Geometric characteristics of a rectangular parallelepiped unit-element (O and o indicate the origin of the global and a local coordinate system, respectively).

resident liquid-phase solute concentration, which is defined as the solute mass per unite volume of interstitial fluid; $C^*(t, \mathbf{Q})$ is the solid-phase or sorbed solute concentration defined as the sorbed solute mass per aquifer solids mass; D_{xx}, D_{yy}, and D_{zz} are the principal hydrodynamic dispersion coefficients; U_x is the average interstitial fluid velocity; Q_x is the spatial coordinate in the direction of flow; t is the time; ρ is the bulk density of the solid matrix; and θ is the porosity. Note that U_x, ρ, θ, and $D_{ij}(i, j = x, y, z)$ are assumed to be scalar, position-independent constants. For linear, reversible, instantaneous sorption, the equilibrium relationship between the solute substance in the aqueous and solid phases is given by

$$C^*(t, \mathbf{Q}) = K_d(\mathbf{q})C(t, \mathbf{Q}), \tag{5}$$

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. In the present analysis, the distribution coefficient and the other geochemical properties of the porous formation possess directional periodicities with spatial periods l_x, l_y, and l_z. Consequently, the distribution coefficient varies within each element. Alternatively, the equilibrium relationship (5) can be written as

$$S^*(t, \mathbf{Q}) = k_d(\mathbf{q})C(t, \mathbf{Q}), \tag{6}$$

where $S^*(t, \mathbf{Q}) = \rho C^*(t, \mathbf{Q})/\theta$ is the solid-phase or sorbed solute concentration with units identical to $C(t, \mathbf{Q})$, and $k_d(\mathbf{q}) = \rho K_d(\mathbf{q})/\theta$ is the dimensionless partition or distribution coefficient. Note that the total mass (in solution and sorbed) in volume

V is $\partial V[C + S^*]$. Combining Equations (4) and (6) leads to

$$R(\mathbf{q}) \frac{\partial C(t, \mathbf{Q})}{\partial t} = D_{xx} \frac{\partial^2 C(t, \mathbf{Q})}{\partial Q_x^2} + D_{yy} \frac{\partial^2 C(t, \mathbf{Q})}{\partial Q_y^2} + D_{zz} \frac{\partial^2 C(t, \mathbf{Q})}{\partial Q_z^2} - U_x \frac{\partial C(t, \mathbf{Q})}{\partial Q_x},$$

(7)

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

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

(8)

For an unbounded porous medium in which an amount of solute mass W is instantaneously injected at $t = 0$ at the point $\mathbf{Q}^0 = \mathbf{Q}_{n0} + \mathbf{q}^0$, the appropriate initial and boundary conditions that lead to correct evaluation of resident liquid-phase concentrations are (Kreft and Zuber, 1978)

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

(9)

$$\lim_{|\mathbf{Q} - \mathbf{Q}^0| \to \infty} C(t, \mathbf{Q}) = \lim_{|\mathbf{Q}_n - \mathbf{Q}_{n0}| \to \infty} C(t, \mathbf{Q}) = 0,$$

(10)

where δ_{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 (10) holds, because $|\mathbf{q} - \mathbf{q}^0| = O(l_i)$ (Brenner, 1980b). Furthermore, we impose 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)

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

(11)

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

(12)

where $\nabla_q = [\partial/\partial q_x, \partial/\partial q_y, \partial/\partial q_z]^T$ is the vector differential operator. The retardation factor is modelled as periodic, which means that for any $\mathbf{q}$ in the interior or the boundary of the unit element

$$R(\mathbf{q}) = R(\mathbf{q} + \mathbf{l}_i).$$

(13)

$R(\mathbf{q})$ as well as its derivatives are also continuous at any point on the six faces of each parallelepiped unit element

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

(14)

$$\nabla_q R(\mathbf{Q}_n, \mathbf{q}) = \nabla_q R(\mathbf{Q}_n - \mathbf{l}_i, \mathbf{q} + \mathbf{l}_i), \quad (\mathbf{q} \in \partial \mathbf{q}_i).$$

(15)

Note that in Equations (11), (12), (14), and (15), the vector $\mathbf{q}$ is on an interface of two consecutive unit elements. For vectorial representation of the conditions (11) through (15) refer to the definition-sketch in Figure 1.

The solute concentration can also be interpreted as a probability density function by setting $W = 1$: $C(t, \mathbf{Q}_n, \mathbf{q}|\mathbf{Q}_{n0}, \mathbf{q}^0)$ equals to the probability density function of the location of a particle at time t given that at time $t = 0$ it was located at point

(Q_{n^0}, q^0) (Brenner, 1980a, b). Hereafter, for notational convenience it is assumed that $Q_{n^0} = 0$ and $q^0 = 0$, where 0 is the null vector and indicates the origin of the unit element defined by $\{n^0\} = \{0, 0, 0\}$.

4. Method of 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 Taylor–Aris–Brenner dispersion theory, the local spatial moments of the liquid-phase solute concentration or probability density function are defined as

$$\mathbf{m}_m(t, \mathbf{q}) = \sum_n \mathbf{Q}_n^m C(t, \mathbf{Q}_n, \mathbf{q}), \quad (m = 0, 1, 2, \ldots), \tag{16}$$

where

$$\sum_n \overset{\text{def}}{=} \sum_{n_x = -\infty}^{\infty} \sum_{n_y = -\infty}^{\infty} \sum_{n_z = -\infty}^{\infty}, \tag{17}$$

$\mathbf{Q}_n^m = \mathbf{Q}_n \cdots \mathbf{Q}_n$ (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 ijth element is the product of the i and j element of $\mathbf{Q}_n$; and so on. The global moments of the liquid-phase solute concentration are defined as

$$\mathbf{M}_m(t) = \int_{V_o} \mathbf{m}_m(t, \mathbf{q}) d^3\mathbf{q} = \sum_n \mathbf{Q}_n^m \check{C}_n(t), \quad (m = 0, 1, 2, \ldots), \tag{18}$$

where

$$\check{C}_n(t) \overset{\text{def}}{=} \int_{V_o} C(t, \mathbf{Q}_n, \mathbf{q}) d^3\mathbf{q}, \tag{19}$$

V_o is the domain of a unit element; $d^3\mathbf{q}$ is a differential volume within a unit element; and $\check{C}_n(t)$ is the liquid-phase solute mass present within the nth 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^0th unit element where solute was introduced instantaneously as a point source.

Similarly, the local moments for the solid-phase or sorbed solute concentration are defined as

$$\mathbf{p}_m(t, \mathbf{q}) = \sum_n \mathbf{Q}_n^m S^*(t, \mathbf{Q}_n, \mathbf{q}), \quad (m = 0, 1, 2, \ldots), \tag{20}$$

and the global moments are defined as

$$\mathbf{P}_m(t) = \int_{V_o} \mathbf{p}_m(t, \mathbf{q}) d^3\mathbf{q} = \sum_n Q_n^m \check{S}_n^*(t), \quad (m = 0, 1, 2, \ldots), \tag{21}$$

where

$$\check{S}_n^*(t) \overset{\text{def}}{=} \int_{V_o} S^*(t, \mathbf{Q}_n, \mathbf{q}) d^3\mathbf{q} \tag{22}$$

is the mass of the solute sorbed within the nth 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 (7) in terms of local coordinates, multiplying the resulting equation by Q_n^m and then summing over all unit elements. Explicitly,

$$\sum_n Q_n^m \left\{ R(\mathbf{q}) \frac{\partial C(t, \mathbf{Q}_n, \mathbf{q})}{\partial t} - D_{xx} \frac{\partial^2 C(t, \mathbf{Q}_n, \mathbf{q})}{\partial q_x^2} - D_{yy} \frac{\partial^2 C(t, \mathbf{Q}_n, \mathbf{q})}{\partial q_y^2} \right.$$

$$\left. - D_{zz} \frac{\partial^2 C(t, \mathbf{Q}_n, \mathbf{q})}{\partial q_z^2} + U_x \frac{\partial C(t, \mathbf{Q}_n, \mathbf{q})}{\partial q_x} \right\} = 0. \tag{23}$$

Since U_x as well as D_{ij} $(i, j = x, y, z)$ are constants, and $R(\mathbf{q})$ is independent of n, Equation (23) may be written as

$$R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} = D_{xx} \frac{\partial^2 \mathbf{m}_m}{\partial q_x^2} + D_{yy} \frac{\partial^2 \mathbf{m}_m}{\partial q_y^2} + D_{zz} \frac{\partial^2 \mathbf{m}_m}{\partial q_z^2} - U_x \frac{\partial \mathbf{m}_m}{\partial q_x}, \tag{24a}$$

or in matrix/vector notation as

$$R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} = \nabla_\mathbf{q} \cdot \{ \mathbf{D} \cdot \nabla_\mathbf{q} \mathbf{m}_m - \mathbf{U} \mathbf{m}_m \}, \tag{24b}$$

where

$$\mathbf{D} = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}, \qquad \mathbf{U} = \begin{pmatrix} U_x \\ 0 \\ 0 \end{pmatrix}, \tag{25a,b}$$

are the dispersion coefficient tensor and velocity vector, respectively.

In addition to Equation (24), the local moments satisfy certain boundary conditions imposed at the unit-element surfaces. These conditions are derived from Equations (11), (12), and (16) and are expressed in terms of 'local jumps' as follows (Brenner, 1980b; Brenner and Adler, 1982; Dill and Brenner, 1982, 1983; Shapiro and Brenner, 1988):

$$[\![m_0]\!] = 0, \qquad [\![\nabla_\mathbf{q} m_0]\!] = 0; \tag{26a,b}$$

$$[\![\mathbf{m}_1]\!] = -[\![\mathbf{q} m_0]\!], \qquad [\![\nabla_\mathbf{q} \mathbf{m}_1]\!] = -[\![\nabla_\mathbf{q} (\mathbf{q} m_0)]\!]; \tag{27a,b}$$

$$[\![\mathbf{m}_2]\!] = \left[\!\!\left[\frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right]\!\!\right], \qquad [\![\nabla_\mathbf{q} \mathbf{m}_2]\!] = \left[\!\!\left[\nabla_\mathbf{q} \left(\frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right) \right]\!\!\right] \tag{28a,b}$$

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

$$[\![F]\!] = F(\mathbf{q} + \mathbf{l}_i) - F(\mathbf{q}), \quad (\mathbf{q} \in \partial \mathbf{q}_i), \tag{29}$$

where 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 (6) in terms of local coordinates, multiplying the resulting equation by Q_n^m and then summing over all unit elements. Explicitly,

$$\mathbf{p}_m = k_d(\mathbf{q})\mathbf{m}_m \tag{30}$$

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

Integrating both sides of Equation (24b) over the domain of a unit element and applying the divergence theorem leads to

$$\int_{V_o} R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} d^3\mathbf{q} = \int_{\partial V_o} \{ \mathbf{D} \cdot \nabla_\mathbf{q} \mathbf{m}_m - \mathbf{U}\mathbf{m}_m \} \cdot \mathbf{n}_s ds, \tag{31}$$

where ∂V_o is the external surface area of a unit element, $\mathbf{n}_s$ is the outward unit vector normal to ∂V_o, and ds is an infinitesimal surface area on ∂V_o. Since each rectangular parallelepiped unit-element consists of six faces,

$$\partial V_o \overset{\text{def}}{=} \sum_i (s_{+i} \oplus s_{-i}), \quad (i = x, y, z), \tag{32}$$

where $s_{\pm i}$ denotes the faces of the unit element, while the plus or minus sign permits identification of equivalent but opposite faces. For example, s_{+x} is the downstream face of a unit element on the $q_y - q_z$ plane, and s_{-x} is the opposite face. Because the unit element is a parallelepiped, $s_{+i} = s_{-i}$. A surface integral over the area of a unit element can also be written in terms of local jumps as (Brenner, 1980b)

$$\int_{\partial V_o} \mathbf{F} \cdot \mathbf{n}_s ds = \sum_i \int_{s_{+i}} [\![\mathbf{F}]\!] \cdot \mathbf{n}_s ds \quad (i = x, y, z). \tag{33}$$

Substitution of the preceding identity into Equation (31) yields

$$\int_{\partial V_o} R(\mathbf{q}) \frac{\partial \mathbf{m}_m}{\partial t} d^3\mathbf{q} = \sum_i \int_{s_{+i}} \{ \mathbf{D} \cdot [\![\nabla_\mathbf{q}\mathbf{m}_m]\!] - \mathbf{U}[\![\mathbf{m}_m]\!] \} \cdot \mathbf{n}_s ds \tag{34}$$

5. Asymptotic Behavior

5.1. ZERO-ORDER MOMENTS

For $m = 0$ the steady-state solution to Equation (24) subject to jump boundary conditions (26a, b) is by inspection deduced to be

$$m_0 = \text{const.} \tag{35}$$

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

$$M_0 + P_0 = W.$$ (36)

Employing the definitions of the global moments and Equation (30), the conservation of mass relationship may be rewritten as

$$\int_{V_o} [m_0 + m_0 k_d(\mathbf{q})] d^3\mathbf{q} = W.$$ (37)

Since at large-time m_0 is a position-independent constant (see Equation (35)), in view of Equation (8) the zero-order local moment for the liquid-phase solute concentration is given by

$$m_0 = \frac{W}{l_x l_y l_z \bar{R}},$$ (38)

where the dimensionless variable

$$\bar{R} \stackrel{\text{def}}{=} \frac{1}{l_x l_y l_z} \int_{V_o} R(\mathbf{q}) d^3\mathbf{q} = \text{const.},$$ (39)

is the retardation factor averaged over the volume of a unit element. Substitution of (38) into (18) yields the liquid-phase zero-order global moment

$$M_0 = \frac{W}{\bar{R}}.$$ (40)

5.2. FIRST-ORDER MOMENTS

For $m = 1$, Equation (34) can be written as

$$\int_{V_o} R(\mathbf{q}) \frac{\partial \mathbf{m}_1}{\partial t} d^3\mathbf{q} = \sum_i \int_{s_{+i}} \mathbf{U}[\![\mathbf{q} m_0]\!] \cdot \mathbf{n}_s ds = \int_{V_o} \nabla_\mathbf{q} \cdot \{\mathbf{U} \mathbf{q} m_0\} d^3\mathbf{q},$$ (41)

where the local boundary conditions (27a,b), Equation (33) and the divergence theorem have been employed.

Let us now determine the first local moment. Since the velocity vector $\mathbf{U}$ has only one nonzero entry (element), it is evident that $m_{1(y)}, m_{1(z)}$ ultimately become independent of time. One can verify that $m_{1(y)} = [-q_y + \Phi_y]m_0$ and $m_{1(z)} = [-q_z + \Phi_z]m_0$, where $\bar{\Phi}_y$ and $\bar{\Phi}_z$ are constants and m_0 is given from Equation (38), are the solutions. Note that the subscripts in parentheses, (i), indicate the appropriate elements of the corresponding vector $\mathbf{m}_1$. Inspection of boundary conditions (27a, b) suggests for large times a trial solution for the $m_{1(x)}$ element of the first local moment vector of the form

$$m_{1(x)} = [\Gamma t - q_x + \Phi_x(\mathbf{q})] \frac{W}{l_x l_y l_z \bar{R}},$$ (42)

where Γ 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,

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

$$\nabla_\mathbf{q} \Phi_x(\mathbf{q}) = \nabla_\mathbf{q} \Phi_x(\mathbf{q} + \mathbf{l}_i), \quad (\mathbf{q} \in \partial\mathbf{q}_i).$$ (44)

Note that the Equation (42) satisfies the conditions (27a, b). For the $m_{1(x)}$ element, Equation (41) can be written as follows

$$\int_{V_o} R(\mathbf{q}) \frac{\partial m_{1(x)}}{\partial t} d^3\mathbf{q} = U_x m_0 l_x l_y l_z = \frac{U_x W}{R}. \tag{45}$$

Substituting (42) into (45) yields

$$\Gamma = \frac{U_x}{R}. \tag{46}$$

Combining Equations (46) and (42), the general trial solution for any element $m_{1(i)}$ is given by

$$m_{1(i)} = \left[\frac{U_i t}{R} - q_i + \Phi_i(\mathbf{q}) \right] \frac{W}{l_x l_y l_z R}, \quad (i = x, y, z). \tag{47}$$

Employing Equations (18) and (47) yields the expression for the elements of the first global moment

$$M_{1(i)} = \left[\frac{U_i t}{R} - \frac{l_i}{2} + \bar{\Phi}_i \right] \frac{W}{R}, \quad (i = x, y, z), \tag{48}$$

where

$$\bar{\Phi}_i \stackrel{\text{def}}{=} \frac{1}{l_x l_y l_z} \int_{V_o} \Phi_i(\mathbf{q}) d^3\mathbf{q} = \text{const.} \tag{49}$$

To complete the description of the first-order local moments, $\Phi_i(\mathbf{q})$ must be determined. Substituting (47) (for $i = x$) into (24a) and (27a, b) leads to the following set of partial differential equation and local jump conditions

$$(R(\mathbf{q}) - \bar{R}) \frac{U_x}{R} = D_{xx} \frac{\partial^2 \Phi_x(\mathbf{q})}{\partial q_x^2} + D_{yy} \frac{\partial^2 \Phi_x(\mathbf{q})}{\partial q_y^2} + D_{zz} \frac{\partial^2 \Phi_x(\mathbf{q})}{\partial q_z^2} - U_x \frac{\partial \Phi_x(\mathbf{q})}{\partial q_x}, \tag{50}$$

$$[\![\Phi_x(\mathbf{q})]\!] = 0, \tag{51a}$$

$$[\![\nabla_\mathbf{q} \Phi_x(\mathbf{q})]\!] = 0. \tag{51b}$$

Since $R(\mathbf{q})$ is periodic in all three directions, it can be expanded in a Fourier series

$$R(\mathbf{q}) = \bar{R} + \sum_{\mathbf{b} \neq 0} \lambda(\mathbf{b}) \exp[j 2\pi \mathbf{q} \cdot \hat{\mathbf{b}}], \tag{52}$$

where $\lambda(\mathbf{b})$ are known coefficients (the discrete spectrum of $R(\mathbf{q})$), $\mathbf{b}$ is a three dimensional vector of wavenumbers, $\hat{\mathbf{b}} = (\hat{b}_x, \hat{b}_y, \hat{b}_z)^T = (b_x/l_x, b_y/l_y, b_z/l_z)^T$ and $j = \sqrt{-1}$. The solution of (50) which satisfies (51a, b) is a series of the form

$$\Phi_x(\mathbf{q}) = \bar{\Phi}_x + \sum_{\mathbf{b} \neq 0} \mu(\mathbf{b}) \exp[j 2\pi \mathbf{q} \cdot \hat{\mathbf{b}}], \tag{53}$$

where $\mu(\mathbf{b})$ is a spectrum to be obtained by introducing (52) and (53) into the

partial differential equation (50). Hence it follows that

$$\mu(\mathbf{b}) = -\frac{U_x}{R} \frac{\lambda(\mathbf{b})}{[4\pi^2(b_x^2 D_{xx} + b_y^2 D_{yy} + b_z^2 D_{zz}) + j2\pi b_x U_x]}, \quad (\mathbf{b} \neq 0). \tag{54}$$

5.3. SECOND-ORDER MOMENTS

For $m = 2$, Equation (34) can be written as

$$\int_{V_0} R(\mathbf{q}) \frac{\partial \mathbf{m}_2}{\partial t} d^3\mathbf{q} = \sum_i \int_{S_{+i}} \left\{ \mathbf{D} \cdot \left[\nabla_\mathbf{q} \left(\frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right) \right] - \mathbf{U} \left[\frac{\mathbf{m}_1 \mathbf{m}_1}{m_0} \right] \right\} \cdot \mathbf{n}_s ds, \tag{55}$$

where the local unit-element jump boundary conditions (28a, b) have been used. For the element $m_{2(xx)}$, where the double subscripts in parentheses, (ij), indicate the corresponding element of the dyadic $\mathbf{m}_2$, Equation (55) can be written as

$$\int_{V_0} R(\mathbf{q}) \frac{\partial m_{2(xx)}}{\partial t} d^3\mathbf{q} = \frac{1}{m_0} \int_0^{l_y} \int_0^{l_z} \left[D_{xx} \frac{\partial m_{1(x)}^2}{\partial q_x} - U_x m_{1(x)}^2 \right] dq_y dq_z. \tag{56}$$

Substitution of (8) and (47) (for $i = x$) into (56) followed by integral evaluations yields

$$\int_{V_0} [1 + k_d(\mathbf{q})] \frac{\partial m_{2(xx)}}{\partial t} d^3\mathbf{q} = \left(\frac{U_x^2 t}{R} - \frac{U_x l_x}{2} + U_x \bar{\Phi}_x + D_{xx} \right) \frac{2W}{R}. \tag{57}$$

Similar expressions can be derived for all other diagonal elements of $\mathbf{m}_2$. In view of (18), (21), and (30) Equation (57) can be written as

$$\frac{dM_{2(xx)}}{dt} + \frac{dP_{2(xx)}}{dt} = \left(\frac{U_x^2 t}{R} - \frac{U_x l_x}{2} + U_x \bar{\Phi}_x + D_{xx} \right) \frac{2W}{R}. \tag{58}$$

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

$$m_{2(xx)} = [E_{xx} t^2 + Z_{xx}(\mathbf{q})t + H_{xx}(\mathbf{q})] \frac{W}{l_x l_y l_z R}, \tag{59}$$

where E_{xx} is a constant and $Z_{xx}(\mathbf{q})$, $H_{xx}(\mathbf{q})$ are functions of the local coordinates. As will be shown in the next section, evaluation of the term $H_{xx}(\mathbf{q})$ is not necessary for the determination of the dispersion dyadic that governs the macroscopic solute transport process. Also, combining (30) and (59) yields the second local moment of the solid-phase solute concentration for the local equilibrium sorption model

$$p_{2(xx)} = k_d(\mathbf{q})[E_{xx} t^2 + Z_{xx}(\mathbf{q})t + H_{xx}(\mathbf{q})] \frac{W}{l_x l_y l_z R}. \tag{60}$$

Integrating Equations (59) and (60) over the volume of a unit element, the trial

second global moments of the liquid- and solid-phase solute concentrations are

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

(61)

$$P_{2(xx)} = (E_{xx}\bar{k}_d t^2 + \overline{Z_{xx}k_d}t + \overline{H_{xx}k_d})\frac{W}{\bar{R}}.$$

(62)

Substitution of (61) and (62) into (58) followed by some manipulations yields

$$E_{xx} = \frac{U_x^2}{\bar{R}^2}.$$

(63)

Substitution of (38) and (47) (for $i = x$) into the local unit-element jump boundary condition (28a) leads to

$$[\![m_{2(xx)}]\!] = \left[\frac{U_x^2 t^2}{\bar{R}^2} + \frac{2U_x}{\bar{R}}\{\Phi_x(\mathbf{q}) - q_x\}t + \{\Phi_x(\mathbf{q}) - q_x\}^2\right]\frac{W}{l_x l_y l_z \bar{R}}.$$

(64)

Comparison of (59) and (64) suggests that

$$Z_{xx}(\mathbf{q}) = \frac{2U_x}{\bar{R}}[\Phi_x(\mathbf{q}) - q_x] + \frac{2D_{xx}}{\bar{R}} + \frac{2U_x}{\bar{R}^2}\overline{[q_x - \Phi_x(\mathbf{q})]^{\triangleleft}R(\mathbf{q})^{\triangleleft}},$$

(65)

where the term $F^{\triangleleft}$ indicates the value of the function F minus its average over the volume of a unit element ($F^{\triangleleft} = F - \bar{F}$), and the expression for the volume-averaged term is derived in the Appendix. Since all the necessary terms of the second global moment for the liquid-phase solute concentration are evaluated, Equation (61) can be written as

$$M_{2(xx)} = \left[\frac{U_x^2 t^2}{\bar{R}^2} - \frac{U_x l_x t}{\bar{R}} + \frac{2U_x \bar{\Phi}_x t}{\bar{R}} + \frac{2D_{xx}t}{\bar{R}} + \frac{2U_x t}{\bar{R}^2} \times \right.$$
$$\left. \times \overline{[q_x - \Phi_x(\mathbf{q})]^{\triangleleft}R(\mathbf{q})^{\triangleleft}} + \bar{H}_{xx}\right]\frac{W}{\bar{R}}.$$

(66a)

In a similar fashion are derived the expressions for the other two diagonal elements of the dyadic $\mathbf{M}_2$

$$M_{2(yy)} = 2\left(\frac{D_{yy}t}{\bar{R}}\right)\frac{W}{\bar{R}},$$

(66b)

$$M_{2(zz)} = 2\left(\frac{D_{zz}t}{\bar{R}}\right)\frac{W}{\bar{R}}.$$

(66c)

6. Effective Macroscopic Coefficients

The mean or effective macroscopic velocity vector $\overline{\mathbf{U}^{\diamond}}$ and the mean macroscopic dispersion dyadic $\overline{\mathbf{D}^{\diamond}}$ of a Brownian particle are defined by (Brenner, 1980a, b)

$$\overline{\mathbf{U}^{\diamond}} = \lim_{t \to \infty} \frac{d\bar{\mathbf{Q}}_n}{dt},$$

(67)

$$\overline{\mathbf{D}^{\diamond}} = \frac{1}{2} \lim_{t \to \infty} \frac{d\overline{(\mathbf{Q_n} - \overline{\mathbf{Q}_n})^2}}{dt},$$ (68)

where for this study $\overline{\mathbf{Q}_n}$ is the ensemble average of the displacement vector $\mathbf{Q_n}$ normalized with respect to the zeroth global moment, and it is given by

$$\overline{\mathbf{Q}_n} = \frac{1}{M_0} \sum_n \mathbf{Q_n} \check{C}_n(t),$$ (69)

and $\overline{(\mathbf{Q_n} - \overline{\mathbf{Q}_n})^2}$ is the dyadic ensemble mean-square macroscopic displacement $\mathbf{Q_n}$ from $\overline{\mathbf{Q}_n}$ at time t normalized with respect to the zeroth global moment, and it is given by

$$\overline{(\mathbf{Q_n} - \overline{\mathbf{Q}_n})^2} = \frac{1}{M_0} \sum_n (\mathbf{Q_n} - \overline{\mathbf{Q}_n})^2 \check{C}_n(t).$$ (70)

Combining Equations (18) (for $m = 1$) and (69) yields

$$\overline{\mathbf{Q}_n} = \frac{\mathbf{M}_1}{M_0}.$$ (71)

Furthermore, Equations (18) (for $m = 1$), (70) and (71) lead to

$$\overline{(\mathbf{Q_n} - \overline{\mathbf{Q}_n})^2} = \frac{1}{M_0} \sum_n [(\mathbf{Q_n}\mathbf{Q_n} - \mathbf{Q_n}\overline{\mathbf{Q}_n} - \overline{\mathbf{Q}_n}\mathbf{Q_n} + \overline{\mathbf{Q}_n}\overline{\mathbf{Q}_n})\check{C}_n(t)] = \frac{\mathbf{M}_2}{M_0} - \frac{\mathbf{M}_1\mathbf{M}_1}{M_0^2},$$ (72)

It should be noted that the normalization with respect to M_0 could be avoided if injection of a conservative solute having unit mass ($M_0 = 1$, $\forall t \geqslant 0$) or equivalently if a single Brownian particle, is considered. Using Equations (71) and (72), the definitions of $\overline{\mathbf{U}^{\diamond}}$ and $\overline{\mathbf{D}^{\diamond}}$ can be rewritten as follows

$$\overline{\mathbf{U}^{\diamond}} = \lim_{t \to \infty} \frac{d}{dt} \left(\frac{\mathbf{M}_1}{M_0} \right),$$ (73)

$$\overline{\mathbf{D}^{\diamond}} = \frac{1}{2} \lim_{t \to \infty} \frac{d}{dt} \left(\frac{\mathbf{M}_2}{M_0} - \frac{\mathbf{M}_1\mathbf{M}_1}{M_0^2} \right).$$ (74)

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 (40), (48), and (73) the effective velocity vector is

$$\overline{\mathbf{U}^{\diamond}} = \frac{1}{\overline{R}} \begin{pmatrix} U_x \\ 0 \\ 0 \end{pmatrix}$$ (75)

Also, from (40), (48), (66), and (74) it follows that the macrodispersion dyadic is

$$\overline{\mathbf{D}^{\diamond}} = \frac{1}{\overline{R}} \begin{pmatrix} D_{xx}^{\bullet} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix},$$ (76)

where

$$D_{xx}^{\bullet} = D_{xx} + \frac{U_x}{\bar{R}} \overline{[q_x - \Phi_x(\mathbf{q})]^{-1} R(\mathbf{q})^{-1}}. \tag{77}$$

The second term on the right hand side of the preceding equation is the effect of averaging the spatially-periodic distribution coefficient over the volume of a unit element. This contribution to the longitudinal macrodispersion coefficient is commonly referred to as the Taylor dispersion coefficient (Horn, 1971; Valocchi, 1989).

7. Rate-Limited Sorbing Solute Transport

In this section the effective velocity vector and macrodispersion dyadic are derived for the case where sorbing solute transport is no longer under local chemical equilibrium conditions but it is governed by the following first-order reversible sorption kinetic relationship (Valocchi, 1989)

$$\frac{\partial S^*(t, \mathbf{Q})}{\partial t} = k_f(\mathbf{q})C(t, \mathbf{Q}) - k_r(\mathbf{q})S^*(t, \mathbf{Q})$$

$$= k_r(\mathbf{q})[k_d^0(\mathbf{q})C(t, \mathbf{Q}) - S^*(t, \mathbf{Q})], \tag{78}$$

where $k_f(\mathbf{q})$ and $k_r(\mathbf{q})$ are the forward and reverse sorption rate coefficients, and

$$k_d^0(\mathbf{q}) = \frac{k_f(\mathbf{q})}{k_r(\mathbf{q})} \tag{79}$$

is the dimensionless partition or distribution coefficient. The sorption rate coefficients and consequently $k_d^0(\mathbf{q})$ are assumed to possess directional periodicities with spatial periods l_x, l_y, and l_z.

Employing the previously described Taylor–Aris–Brenner method of moments in Equation (4) and (78), leads to

$$\frac{\partial \mathbf{m}_m}{\partial t} + \frac{\partial \mathbf{p}_m}{\partial t} = \nabla_q \cdot \{ \mathbf{D} \cdot \nabla_q \mathbf{m}_m - \mathbf{U} \mathbf{m}_m \}, \tag{80}$$

$$\frac{\partial \mathbf{p}_m}{\partial t} = k_r(\mathbf{q})[k_d^0(\mathbf{q})\mathbf{m}_m - \mathbf{p}_m], \tag{81}$$

where the latter equation is a first-order linear relationship between the local moments for the liquid- and solid-phase concentration.

Following the procedure outlined in Sections 5 and 6, the large-time velocity vector and macrodispersion dyadic become

$$\overline{\mathbf{U}^{\circ}} = \frac{1}{R^0} \begin{pmatrix} U_x \\ 0 \\ 0 \end{pmatrix}, \tag{82}$$

$$\overline{\overline{\mathbf{D}}}^{\diamond} = \frac{1}{\overline{R^0}} \begin{pmatrix} D^{\bullet\bullet}_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix},$$ (83)

where

$$D^{\bullet\bullet}_{xx} = D_{xx} - \frac{U_x}{\overline{R^0}} \overline{[\overline{q}_x - \Phi_x(\mathbf{q})]^{-1} R^0(\mathbf{q})^{-1}} + \frac{U_x^2}{\overline{R^0}^2} \overline{\left(\frac{k^0_d}{k_r}\right)},$$ (84)

$$R^0(\mathbf{q}) = 1 + k^0_d(\mathbf{q}).$$ (85)

The first two terms on the right had side of the preceding equation are the longitudinal hydrodynamic and Taylor dispersion coefficients. However, the third term which is not present in the case of local equilibrium sorption (Equation 77), represents the effect of the first-order reversible kinetic sorption.

It should be noted that, at the limit $\bar{k}_r \to \infty$ which represents local equilibrium conditions at fixed $\bar{k}^0_d$ (Jennings and Kirkner, 1984; Valocchi, 1989), the contribution to longitudinal dispersion from the first-order sorption rate vanishes. Therefore, the kinetic sorption relationship becomes identical to the chemical reversible sorption isotherm, and $D^{\bullet\bullet}_{xx} = D^{\bullet}_{xx}$.

Equation (84) is similar to the result for a perfectly stratified aquifer derived by Valocchi (1989). However, Valocchi's Taylor dispersion and reversible kinetic sorption terms of the longitudinal effective macrodispersion coefficient are averaged over the aquifer depth, while the terms in (84) are averaged over the volume of a unit element. The effective macroscopic coefficients derived in this work are more general, since three-dimensional spatially-periodic sorption is considered.

8. Simulation by Particle Tracking

In order to verify the analytical expressions for the effective or large-time co-efficients governing macroscopic solute transport under local equilibrium conditions, the random walk method is employed. The random walk technique has been applied in numerous solute transport studies (e.g., Ahlstrom *et al.*, 1977; Smith and Schwartz, 1980; Kinzelbach, 1988; Black, 1988). The method is as follows. A large group of particles representing solute mass is displaced by superimposing on the advective movement a random dispersive shift. The magnitude and direction of the dispersive displacements for each individual time step are generated independently from an appropriate probability distribution. According to the central limit theorem, the cumulative outcome of a large number of consecutive runs with an arbitrary probability distribution approximates a Gaussian distribution. Therefore, the precise form of the probability distribution is not important, as long as it yields equivalent variance and mean. For computational simplicity, the uniform distribution is most frequently employed. In the limit of infinitely many particles, their spatial distribution becomes equal to the solute concentration which satisfies the advection-dispersion equation.

We have employed the particle tracking technique for the case where the retardation factor is spatially-periodic only in the x-direction, and can be described by

$$R(\mathbf{q}) = \bar{R} + A \cos(2\pi q_x / l_x), \tag{86}$$

where A is the amplitude of oscillation of the retardation factor. In view of the selected functional relation of the retardation factor, it is evident that Equation (77) reduces to

$$D^{\bullet}_{xx} = D_{xx} + \frac{U_x^2}{\bar{R}^2} \left[\frac{A^2 D_{xx}}{8\pi^2 D_{xx}^2 / l_x^2 + 2U_x^2} \right]. \tag{87}$$

For one thousand particles distributed initially uniformly over the volume of a unit element with $l_x = l_y = l_z = 1m$, we have obtained the rate of change of the first global moment (Figure 2), as well as the rate of change of second-central global moment (Figure 3) for the liquid-phase solute concentration. The parameter values employed in the particle-tracking numerical simulations are $U_x = 5$, $U_y = U_z = 0$ m/d; $D_{xx} = 0.06$, $D_{yy} = 0.03$, $D_{zz} = 0.02$ m^2/d; $\bar{R} = 29$; and $A = 28$. Together with the numerical data we have plotted the theoretical results (solid-lines). The agreement between the numerical and theoretical predictions is good, as seen in Figures 2 and 3. It is apparent that a spatially-variable retardation factor increases the solute spreading significantly. This phenomenon has been explored further by Chrysikopoulos et al. (1990), and it is also demonstrated through the particle-tracking simulations shown in Figure 4. For the particular conditions employed in this simulation, the rate of change of the second-central moment for spatially-
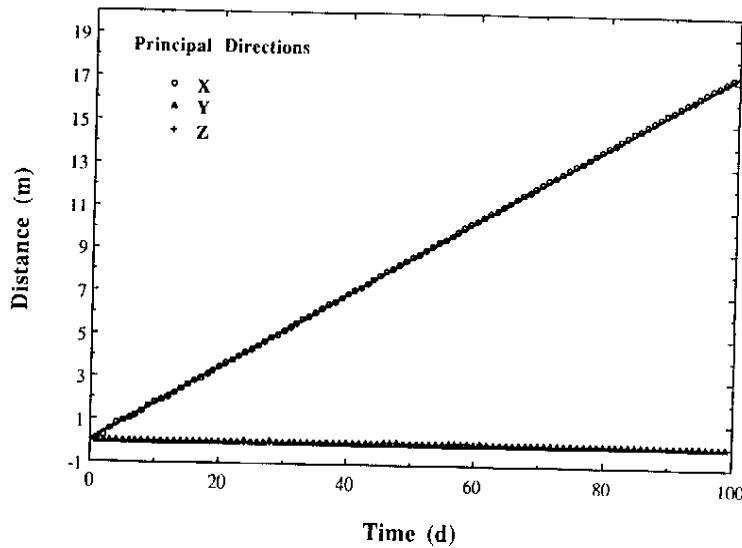

Fig. 2. Rate of change of the first global moment for the liquid-phase solute concentration as computed from theory (solid lines), and from a particle-tracking simulation (symbols).
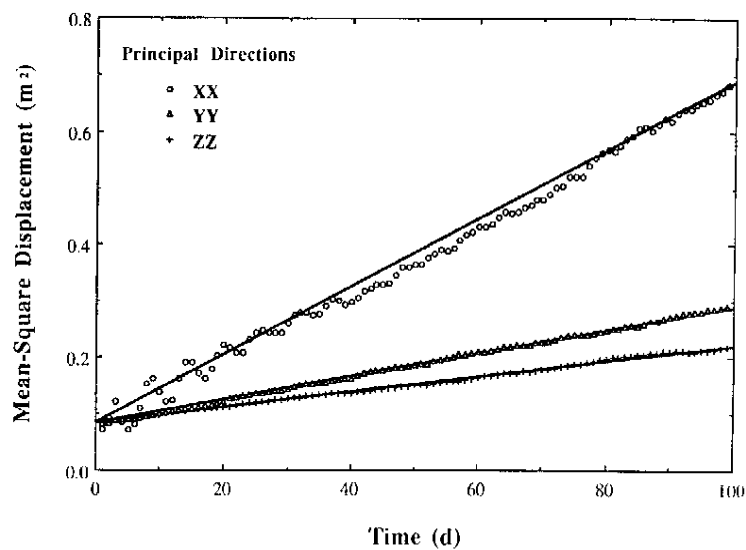
Fig. 3 Rate of change of the second-central global moment for the liquid-phase solute concentration as computed from theory (solid lines), and from a particle-tracking simulation (symbols).
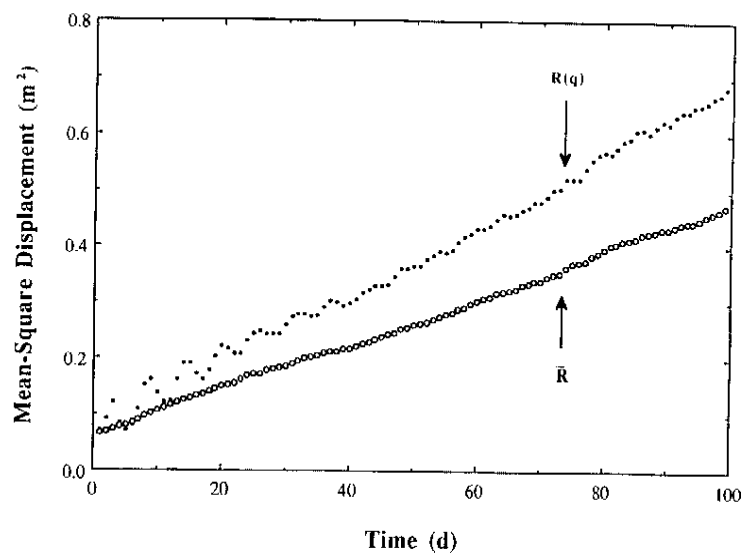

Fig. 4. Comparison of the rate of change of the second-central global moment in the xx-direction, obtained by the random walk model, for spatially-periodic (●), and constant (○) retardation factors.

periodic retardation factor is approximately 50% larger than the case of invariant retardation factor, $\bar{R}$.

9. Summary and Conclusions

Expressions for the macroscopic velocity vector and dispersion dyadic were derived with the generalized method of Taylor–Aris dispersion. A three-dimensional homogeneous porous medium under the ideal condition of unidirectional flow was considered, mainly to improve our conceptual understanding of the effects of spatial sorption. However, in a similar fashion, the more general problem of spatially-variable flow can be solved without too much additional effort. A chemical equilibrium isotherm as well as a first-order reversible sorption relationship were employed in the present analysis. Under the assumption of local equilibrium sorption it was shown that asymptotically the solute plume is transported with a velocity equal to the unidirectional fluid velocity divided by the average retardation factor. The longitudinal element of the dispersion dyadic was shown to consist of two terms. The first term is the hydrodynamic longitudinal dispersion coefficient divided by the averagte retardation factor, while the second term is the contribution of averaging the locally variable partition coefficient. The other two elements of the dispersion dyadic are just the corresponding principal hydrodynamic dispersion coefficients divided by the average retardation factor. For the case of first-order reversible kinetic sorption, similar results were derived for both the effective velocity vector and dispersion dyadic. However, the longitudinal element of the dispersion dyadic was shown to have a third term expressing the effect of the first-order sorption rate. Therefore, the asymptotic spreading of a sorbing solute plume is critically affected by the spatial variability of the sorption coefficient or retardation factor, as well as by the sorption rate of the solute if local chemical equilibrium conditions are not applicable. Good agreement was shown between the theoretical predictions obtained for the local chemical equilibrium conditions and the particle tracking numerical experimentations.

10. Appendix: Derivation of the Volume-averaged Term in the Taylor Dispersion Coefficient

In this appendix, we develop the expression for the volume-averaged term that appears in the Taylor dispersion coefficient. By definition

$$\overline{[q_x - \Phi_x(\mathbf{q})]^{<1}R(\mathbf{q})^{<1}} \overset{\text{def}}{=} \frac{1}{l_x l_y l_z} \int_{V_o} [q_x - \Phi_x(\mathbf{q})]^{<1} R(\mathbf{q})^{<1} d^3\mathbf{q}, \tag{A1}$$

where

$$q_x^{<1} = q_x - \bar{q}_x, \tag{A2}$$

$$R(\mathbf{q})^{-1} = \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq 0}} \lambda(\mathbf{b}) \exp[j2\pi\mathbf{q} \cdot \mathbf{b}], \tag{A3}$$

$$\Phi_x(\mathbf{q})^{-1} = -\frac{U_x}{R} \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq 0}} \frac{\lambda(\mathbf{b}) \exp[j2\pi\mathbf{q} \cdot \mathbf{b}]}{4\pi^2(b_x^2 D_{xx} + b_y^2 D_{yy} + b_z^2 D_{zz}) + j2\pi b_x U_x}. \tag{A4}$$

Combining Equations (A1) through (A4) and assuming that integrations and summations are interchangeable leads to

$$\overline{[q_x - \Phi_x(\mathbf{q})]^{-1} R(\mathbf{q})^{-1}} = \frac{1}{l_x l_y l_z} \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq 0}} \left\{ \lambda(\mathbf{b}) \int_{V_o} (q_x - \bar{q}_x) \exp[j2\pi\mathbf{q} \cdot \mathbf{b}] d^3q + \right.$$
$$\left. + \frac{U_x}{R} \int_{V_o} \frac{\lambda(\mathbf{b})\lambda^\dagger(\mathbf{b})}{4\pi^2(b_x^2 D_{xx} + b_y^2 D_{yy} + b_z^2 D_{zz}) - j2\pi b_x U_x} d^3q \right\}. \tag{A5}$$

Note that $\lambda(\mathbf{b})$ and $\lambda^\dagger(\mathbf{b})$ are complex conjugates. The integral of the first term on the right-hand side of Equation (A5) is:

$$\int_{V_o} (q_x - \bar{q}_x) \exp[j2\pi\mathbf{q} \cdot \mathbf{b}] d^3q = 0. \tag{A6}$$

Substituting Equation (A6) into (A5) and evaluating the integral of the second term on the right-hand side of Equation (A5), yields the following expression

$$\overline{[q_x - \Phi_x(\mathbf{q})]^{-1} R(\mathbf{q})^{-1}} = \sum_{\substack{\mathbf{b} \\ \mathbf{b} \neq 0}} \frac{U_x \lambda(\mathbf{b})\lambda^\dagger(\mathbf{b})}{[4\pi^2(b_x^2 D_{xx} + b_y^2 D_{yy} + b_z^2 D_{zz}) - j2\pi b_x U_x]R}. \tag{A7}$$

Acknowledgements

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