Volume averaging for determining the effective dispersion tensor: closure using periodic unit cells and comparisons with ensemble averaging

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[1] In this work, we use the method of volume averaging to determine the effective dispersion tensor for a heterogeneous porous medium; closure for the averaged equation is obtained by solution of a concentration deviation equation over a periodic unit cell. Our purpose is to show how the method of volume averaging with closure can be rectified with the results obtained by other upscaling methods under particular conditions. Although this rectification is something that is generally believed to be true, there has been very little research that explores this issue explicitly. We show that under certain limiting (but mild) assumptions, the closure problem provides a Fourier series solution for the effective dispersion tensor. When second-order spatial stationarity is imposed on the velocity field, the method yields a simple Fourier series that converges to an integral form in the limit as the period of the unit cell approaches infinity. This limiting result is identical to the quasi-Fickian forms that have been developed previously via ensemble averaging by *Deng et al.* [1993] and recently by *Fiori and Dagan* [2000] except in the definition of the averaging operation. As a second objective we have conducted a numerical study to evaluate the influence of the size of the averaging volume on the effective dispersion tensor and its volume averaged statistics. This second objective is complimentary in many ways to recent research reported by *Rubin et al.* [1999] (via ensemble averaging) and by *Wang and Kitanidis* [1999] (via volume averaging) on the block-averaged effective dispersion tensor. The variability of the effective dispersion tensor from realization to realization is assessed by computing the volume-averaged effective dispersion tensor for an ensemble of finite fields with the same (ensemble) statistics. Ensembles were generated using three different sizes of unit cells. All three unit cell sizes yield similar results for the value of the mean effective dispersion tensor. However, the coefficient of variation depends strongly upon the size of the unit cell, and our results are consistent with those developed by *Fiori* [1998] from the ensemble averaging perspective. This implies that in applications the actual value of the effective dispersion tensor may be significantly different than expected on the basis of unconditioned hydraulic conductivity statistics, and this variation should be considered when applying macrodispersion to real-world systems. *INDEX TERMS:* 1829 Hydrology: Groundwater hydrology; 1832 Hydrology: Groundwater transport; 1869 Hydrology: Stochastic processes; *KEYWORDS:* volume averaging, upscaling, subsurface transport, stochastic hydrology, contaminant hydrology

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1. Introduction

[2] The problem of developing the macroscopic-scale description of solute transport in heterogeneous media has been approached from many different mathematical perspectives including (among others): Eulerian perturbation analysis [*Gelhar*, 1993], Eulerian nonlocal transport theory [*Deng et al.*, 1993; *Cushman*, 1997], Lagrangian perturbation analysis [e.g., *Dagan*, 1984, 1989; *Fiori and Dagan*, 2000], volume averaging [e.g., *Cushman*, 1984; *Kitanidis*, 1988; *Plumb and Whitaker*, 1988; *Gray et al.*, 1993; *Ahmadi and Quintard*, 1996; *Quintard and Whitaker*, 1998b; *Whitaker*, 1999; *Wang and Kitanidis*, 1999], cumulant expansion [e.g., *Kabala and Sposito*, 1991; *Kavvas and Karakas*, 1996; *Wood*, 1998; *Wood and Kavvas*, 1999], semi-group theory [*Neuman*, 1993], renormalization group theory [*Jaekel and Vereecken*, 1997], homogenization theory [e.g., *Mauri*, 1991; *Auriault and Adler*, 1995; *Panfilov*, 2000], and moment-matching methods [e.g., *Shapiro and Brenner*, 1988; *Brenner and Edwards*, 1993; *Edwards et al.*, 1993]. Although there has been much discussion about the

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differences among the methods, the goals of each are essentially the same: (1) to develop the form of the macroscopic-scale transport equations that describe the evolution of the concentration field statistics (the average concentration, concentration variance, plume moments, etc.), and (2) to relate the underlying microscopic-scale structure and physical properties to the associated effective parameters (or sometimes the "equivalent parameters" in the sense of *Renard and De Marsily* [1997]) that appear in the macroscopic transport equations.

[3] The physical processes that lead to macrodispersion are the same regardless of the mathematical approach that is adopted. It is the variations in the velocity field (at the pore scale and above) that combine with molecular diffusion to create spreading of an initial solute distribution. In principle then, any consistent mathematical approach, subject to a uniform set of approximations or constraints, should lead to essentially the same description of the macroscopic spreading phenomenon. Some of the differences among the various approaches, particularly between the Eulerian and Lagrangian ensemble averaging perspectives, have recently begun to be rectified by the recognition that the Darcy-scale hydrodynamic dispersion can have a significant effect upon macrodispersion [e.g., *Cushman et al.*, 1996; *Fiori*, 1996; *Fiori and Dagan*, 2000].

[4] Although the method of volume averaging has been used extensively in chemical engineering, it has not been as widely employed in subsurface hydrology. Notable exceptions include the works of *Cushman* [1984], *Gray et al.* [1993], *Kitanidis* [1988, 1992], *Plumb and Whitaker* [1988], *Chrysikopoulos et al.* [1992], and *Quintard and Whitaker* [1994a, 1994b, 1994c, 1998a, 1998b]. In this paper, we use volume averaging with closure to develop a series solution (which becomes an integral solution in the limit of increasing averaging volume) for the effective dispersion tensor. The closure problem is developed for a spatially periodic system of unit cells, and the solution is found through the use of a finite Fourier transform method. For second-order spatially stationary log conductivity fields that are large enough, the solution tends toward the ensemble average quasi-Fickian results that have been obtained by *Deng and Cushman* [1995a] and by *Fiori and Dagan* [2000]. Finally, the effective dispersion tensor is computed numerically for various realizations of the random conductivity field and for increasing sizes of the averaging volume. Results from these numerical simulations are compared with closed form solutions that have been developed by *Fiori* [1998] and *Fiori and Dagan* [2000]. Our work is complimentary to recent results developed by *Rubin et al.* [1999] on the block-effective macrodispersivity calculated via ensemble averaging with a high wave number cutoff, and complimentary to work by *Wang and Kitanidis* [1999] who determined the asymptotic value of the dispersion tensor via volume averaging. The results reported in our work are unique in that (1) they establish a direct connection between the preasymptotic dispersion tensor predicted from the volume averaging and ensemble averaging perspectives, and (2) estimates of the variability in the effective dispersion tensor as a function of averaging volume size are presented. Our calculations show that the coefficient of variation of the effective dispersion tensor depends strongly upon the size of the unit cell, even if the mean value of the effective dispersion tensor is not greatly affected by the size of the averaging volume, and this result is consistent with the analysis of *Fiori* [1998]. Because ergodic arguments are usually invoked (allowing the interchange of ensemble and volume averages) in the application of most ensemble averaging theory, this result has direct implications for the interpretation of field data. The primary implication is that the effective dispersion tensor that is observed in the field may deviate significantly from the ensemble average, even if the underlying field is spatially stationary and the associated solute plume extends over many integral scales of the conductivity field.

[5] The paper is structured as follows. In section 2 we describe the process of volume averaging the Darcy-scale equations for transport to obtain an unclosed equation describing transport at the macroscopic scale. In section 3, we describe how the closure problem can be formulated for periodic unit cells. In section 4, we develop an analytical expression for the effective dispersion tensor in a periodic unit cell using the method of finite Fourier transforms. This expression holds for any finite-sized volume, with the only restrictions being the separation of length-scales and the smallness of the variance of the log conductivity field. We show, further, that as the size of the averaging volume tends toward infinity, the effective dispersion tensor approaches the value derived earlier by *Deng and Cushman* [1995a] and *Fiori and Dagan* [2000]. In section 5, we examine how much variance there is in the value of the effective dispersion tensor for individual realizations of a lognormal hydraulic conductivity field by numerical simulations of the closure problem. These results are compared with the results of *Fiori* [1998] and *Fiori and Dagan* [2000]. We discuss these results in section 6, and finally in section 7 we offer a summary.

2. Volume Averaging of the Local Transport Equation

[6] The starting point for our analysis is the Darcy-scale (REV-scale) transport equation. Although not a requirement for the method of volume averaging [cf. *Quintard and Whitaker*, 1998a, 1998b], we will assume conditions of steady flow so that the continuity and solute transport equations take the form

$$\nabla \cdot (n\mathbf{v}(\mathbf{x})) = 0 \tag{1}$$

$$n\frac{\partial c}{\partial t} = -\nabla \cdot (n\mathbf{v}(\mathbf{x})c) + \nabla \cdot (n\mathbf{D}(\mathbf{x}) \cdot \nabla c) \tag{2}$$

Here n represents the porosity, c the intrinsic Darcy-scale concentration, $\mathbf{v}$ the intrinsic Darcy-scale velocity, and $\mathbf{D}$ the Darcy-scale dispersion tensor. Detailed discussions of the derivation of these equations by upscaling from the pore-scale are given by *Carbonell and Whitaker* [1983], *Dagan* [1989], *Brenner and Edwards* [1993], and *Whitaker* [1999]. Using equation (1), and assuming that variations in the porosity can be neglected, equation (2) can be simplified to

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}(\mathbf{x})c) + \nabla \cdot (\mathbf{D}(\mathbf{x}) \cdot \nabla c) \tag{3}$$

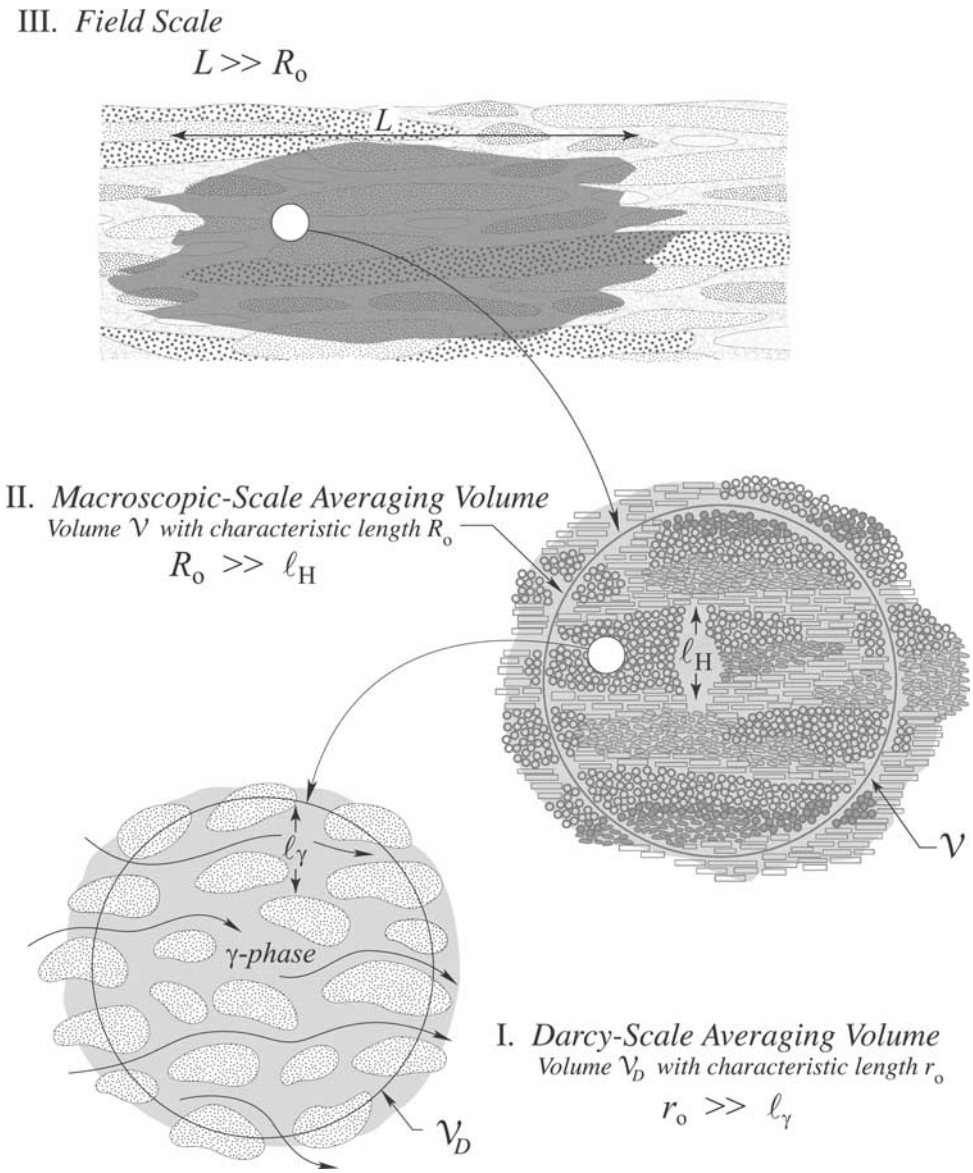

Figure 1. Hierarchical porous medium.

When significant variations in the porosity are encountered, this simplification may not be appropriate and one needs to consider the more detailed analysis of *Quintard et al.* [2001].

[7] In most studies of upscaling transport process for heterogeneous media, equation (3) is adopted (with $\mathbf{v}(\mathbf{x})$ and $\mathbf{D}(\mathbf{x})$ treated as random fields) as the starting point and it is assumed to hold pointwise. The term pointwise is understood to mean the center of a representative volume (REV) of porous media that defines the Darcy scale (the volume $\mathcal{V}_D$ illustrated at level I in Figure 1). The goal of the next level of upscaling is to develop a macroscopic description of the transport process by averaging over a volume (the volume $\mathcal{V}$ illustrated at level II in Figure 1) that is large compared to the characteristic length scale of the Darcy-scale heterogeneities. This length scale is illustrated by ℓ_H in Figure 1. The effective parameters in the macroscopic transport equation are determined from the Darcy-scale details. In principle, both the detailed geometrical structure and physical properties of the Darcy-scale field can influence the effective parameters that appear in the macroscopic transport equation. However, it is often assumed that the structure of the heterogeneity is such that only the statistics of the underlying field are required in order to faithfully describe the dispersion process. For such fields, a macroscopic transport equation can be developed from which the Darcy-scale variability has been filtered, the effects of the Darcy-scale variability being captured through the definition of an effective dispersion tensor. (There is a related issue regarding how one interprets the meaning of the effective dispersion tensor in terms of dilution of the concentration field [e.g., *Kitanidis*, 1994; *Pannone and Kitanidis*, 1999]; we are not addressing this issue in our work.)

[8] For the method of volume averaging, the upscaling filter is a spatial rather then ensemble average. Although volume averaging can be cast in the context of distribution theory in which the generalized density functions can be

interpreted as instrument response functions [*Baveye and Sposito*, 1984; *Cushman*, 1984; *Beckie*, 2001], we will adopt a uniform weighting function. Then, the large-scale volume average can be defined by

$$\langle c \rangle = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} c \, dV \tag{4}$$

where $\mathcal{V}$ represents the macroscopic, or large-scale averaging volume illustrated in Figure 1. With the aid of the definition given by equation (4), we can form the volume average of equation (3) to obtain

$$\left\langle \frac{\partial c}{\partial t} \right\rangle = \langle \nabla \cdot [\mathbf{D}(\mathbf{x}) \cdot \nabla c] \rangle - \langle \nabla \cdot (\mathbf{v}(\mathbf{x}) c) \rangle \tag{5}$$

Using the general transport and the spatial averaging theorems [*Howes and Whitaker*, 1985; *Gray et al.*, 1993], integration and differentiation can be interchanged leading to

$$\frac{\partial \langle c \rangle}{\partial t} = \nabla \cdot \langle \mathbf{D}(\mathbf{x}) \cdot \nabla c \rangle - \nabla \cdot \langle \mathbf{v}(\mathbf{x}) c \rangle \tag{6}$$

In order to simplify the convective term in this result, we make use of the spatial decompositions

$$c = \langle c \rangle + \tilde{c} \tag{7a}$$

$$\mathbf{v}(\mathbf{x}) = \langle \mathbf{v}(\mathbf{x}) \rangle + \tilde{\mathbf{v}}(\mathbf{x}) \tag{7b}$$

from which we can develop the following relation for the volume averaged convective transport term

$$\langle \mathbf{v}(\mathbf{x}) c \rangle = \langle \langle \mathbf{v}(\mathbf{x}) \rangle \langle c \rangle \rangle + \langle \langle \mathbf{v}(\mathbf{x}) \rangle \tilde{c} \rangle + \langle \tilde{\mathbf{v}}(\mathbf{x}) \langle \tilde{c} \rangle \rangle + \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{8}$$

Under the conditions that the characteristic size of the averaging volume, R_o, is sufficiently small compared with the characteristic large-length scale, L, i.e.,

$$(R_o/L)^2 \ll 1 \tag{9}$$

then it is permissible to remove averages from within averages. This simplification can be expressed explicitly for a general function $\langle \psi \rangle$ as

$$\langle \langle \psi \rangle \rangle|_{\mathbf{x}} = \langle \psi \rangle|_{\mathbf{x}} \tag{10}$$

For volume averages, equation (10) is not an identity as it is in ensemble averaging, but an approximation. When equation (10) is applied to the velocity field, it is equivalent to the assumption of quasi-stationarity proposed by *Riley and Corrsin* [1974] [see also *Christakos*, 1992, chap. 2.6]. In section A1 we show that equation (10) is a valid approximation when there is a separation of length scales of the type indicated by equation (9). One should note that this is an overly-conservative constraint by construction, and, although not stated as such, it is identical to a constraint proposed by *Dagan* [1989, sect. 1.10, 2.2.32] for his conceptualization of quasi-stationarity.

[9] If it is assumed that variations of volume averaged quantities are negligible within the averaging volume then equation (8) can be simplified further to the form

$$\langle \mathbf{v}(\mathbf{x}) c \rangle = \langle \mathbf{v}(\mathbf{x}) \rangle \langle c \rangle + \langle \mathbf{v}(\mathbf{x}) \rangle \langle \tilde{c} \rangle + \langle \tilde{\mathbf{v}}(\mathbf{x}) \rangle \langle c \rangle + \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{11}$$

In addition to equation (9), in section A2 we show that equation (11) also allows us to impose the restrictions

$$\langle \langle \mathbf{v}(\mathbf{x}) \rangle \tilde{c} \rangle \ll \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{12a}$$

$$\langle \tilde{\mathbf{v}}(\mathbf{x}) \langle c \rangle \rangle \ll \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{12b}$$

Under these conditions, the volume averaged convective transport can be expressed as

$$\langle \mathbf{v}(\mathbf{x}) c \rangle = \langle \mathbf{v}(\mathbf{x}) \rangle \langle c \rangle + \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{13}$$

[10] These simplifications, along with the decomposition given by equation (7a), can be used in equation (6) to obtain a volume averaged solute transport equation of the form

$$\frac{\partial \langle c \rangle}{\partial t} = \nabla \cdot (\langle \mathbf{D}(\mathbf{x}) \rangle \cdot \nabla \langle c \rangle) + \nabla \cdot \langle \mathbf{D}(\mathbf{x}) \cdot \nabla \tilde{c} \rangle - \langle \mathbf{v}(\mathbf{x}) \rangle \cdot \nabla \langle c \rangle - \nabla \cdot \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{14}$$

One final simplification of this transport equation can be obtained by imposing the restriction,

$$\nabla \cdot \langle \mathbf{D}(\mathbf{x}) \cdot \nabla \tilde{c} \rangle \ll \nabla \cdot \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{15}$$

and again in section A3 we develop the constraint of the form

$$\sigma_Y^2 \ll 1 \tag{16}$$

in support of this simplification. Note that the discarded term, $\nabla \cdot \langle \mathbf{D}(\mathbf{x}) \cdot \nabla \tilde{c} \rangle$, can contribute to both macrodispersion and to skewness of the plume. The contribution to macrodispersion has been considered by *Quintard et al.* [2001], and additional details regarding the influence of this discarded term can be found in that work. Use of equation (15) allows us to express equation (14) in the simplified but unclosed form given byMacroscopic transport equation (unclosed form)

$$\frac{\partial \langle c \rangle}{\partial t} = \nabla \cdot (\langle \mathbf{D}(\mathbf{x}) \rangle \cdot \nabla \langle c \rangle) - \langle \mathbf{v}(\mathbf{x}) \rangle \cdot \nabla \langle c \rangle - \nabla \cdot \langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle \tag{17}$$

Although equation (17) is a macroscopic-scale expression that contains only averaged quantities, it is not yet closed because we do not have an explicit representation of the quantity $\langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle$ in terms of the averaged concentration. Ultimately, we would like to express the quantity $\langle \tilde{\mathbf{v}}(\mathbf{x}) \tilde{c} \rangle$ in a form that is proportional to $\nabla \langle c \rangle$ so that the final macroscopic is that of a convection-dispersion equation. In

the next section, we describe how a closure problem for the quantity $\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$ can be developed for periodic unit cells.

3. Closure Problem in Periodic Unit Cells

[11] In order to close the volume averaged transport equation, the term $\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$ needs to be expressed in terms of the known parameters of the problem and some function of the averaged concentration, $\langle c\rangle$. For this analysis, the velocity is treated as a parameter field whose statistics or pointwise values are assumed to be known independently. The closure problem then reduces to one of determining the deviation concentration, $\tilde{c}$. From equation (7a), we can see that the averaged and deviation concentrations are related by

$$\tilde{c} = c - \langle c\rangle \tag{18}$$

This relationship suggests that a differential equation for the deviation concentration can be developed by subtracting the volume average transport equation (equation (17)) from the Darcy-scale transport equation (equation (3)). This yields

Transport equation for $\tilde{c}$

$$\underbrace{\frac{\partial\tilde{c}}{\partial t}}_{\text{accumulation}} + \underbrace{\mathbf{v}(\mathbf{x})\cdot\nabla\tilde{c}}_{\text{convection}} - \underbrace{\nabla\cdot(\mathbf{D}(\mathbf{x})\cdot\nabla\tilde{c})}_{\text{dispersion}} = -\underbrace{\tilde{\mathbf{v}}(\mathbf{x})\cdot\nabla\langle c\rangle}_{\text{convective source}} + \underbrace{\nabla\cdot\left(\tilde{\mathbf{D}}(\mathbf{x})\cdot\nabla\langle c\rangle\right)}_{\text{dispersive source}} + \underbrace{\nabla\cdot\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle}_{\text{non-local convection}} \tag{19}$$

in which we have decomposed the dispersion tensor according to

$$\mathbf{D}(\mathbf{x}) = \langle\mathbf{D}(\mathbf{x})\rangle + \tilde{\mathbf{D}}(\mathbf{x}) \tag{20}$$

One should note that in the averaged equation (equation (14)) the term $\nabla\cdot\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$ is a macrodispersion term, while in equation (19) it acts as a nonlocal convection term. We use the term 'nonlocal' here because this term involves the integral of the dependent variable of the differential equation (and hence makes equation (19) technically an integro-differential equation). In order to solve the closure problem specified by equation (19), the problem must be augmented by appropriate initial and boundary conditions. A reasonable initial condition for the spatial deviation concentration would be that $\tilde{c}$ is zero at some reference time everywhere in region III illustrated in Figure 1.

[12] Because the term $\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$ is an integrated value, there is some flexibility in the kinds of boundary conditions that can be used to determine the solution to the closure problem for $\tilde{c}$. In other words, the integrated quantity

$$\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle = \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\,dV \tag{21}$$

is somewhat insensitive to the specific boundary conditions used to determine $\tilde{c}$, provided that the volume $\mathcal{V}$ used to compute the integral is in some sense sufficiently large. Any local solution that produces acceptable values of $\tilde{c}$ can be used to evaluate this integral and thus determine the effective dispersion tensor. One reasonable model might be to impose the condition that the deviations are identically zero on the boundaries. For our purposes, a periodic model of a heterogeneous porous medium will be convenient (and imposes less severe constraints on the problem than, say, a Dirichlet condition would).

[13] In terms of the single periodic unit cell, the local closure problem can then be specified by Closure problem

$$\frac{\partial\tilde{c}}{\partial t} + \mathbf{v}\cdot\nabla\tilde{c} - \nabla\cdot(\mathbf{D}\cdot\nabla\tilde{c}) = -\tilde{\mathbf{v}}\cdot\nabla\langle c\rangle + \nabla\cdot(\tilde{\mathbf{D}}\cdot\nabla\langle c\rangle) + \nabla\cdot\langle\tilde{\mathbf{v}}\,\tilde{c}\rangle \tag{22a}$$

Initial condition

$$\tilde{c}(\mathbf{x}) = 0 \quad \text{at} \quad t = t_o \tag{22b}$$

Periodicity

$$\tilde{c}(\mathbf{x}) = \tilde{c}(\mathbf{x}+\mathbf{l}_i), \quad i = 1,2,3 \tag{22c}$$

A consequence of equation (10) and the decomposition given by equation (7a) is that the average of the deviation is zero, and this provides an additional constraint for the perturbation concentration field

Averaging constraint

$$\langle\tilde{c}(\mathbf{x})\rangle = 0 \tag{22d}$$

[14] The use of a spatially periodic model for closure is often misinterpreted, and some additional comments about this closure scheme are warranted. The use of spatially periodic model does not imply that the results apply only to periodic media or that the structure of the porous media is actually assumed to be periodic (see the discussion by *Renard and de Marsily* [1997, sect. 4.7], *Pickup et al.* [1994], *Chrysikopoulos et al.* [1992], *Wang and Kitanidis* [1999, Appendix A], and *Eames and Bush* [1999]). *Quintard and Whitaker* [1994a, 1994b, 1994c] have shown that equation (4) represents the proper volume average for a disordered system and that periodic models are entirely suitable for the determination of effective transport coefficients associated with disordered systems. For sufficiently large unit cells (relative to the characteristic length of the heterogeneities, ℓ_H) the solution will not be significantly influenced by the boundary conditions. This occurs because information propagating from the boundaries is lost due to the heterogeneous structure of the unit cell [cf. *Ochoa-Tapia et al.*, 1994]. Thus the periodic boundary condition is only a device for obtaining a local solution and it is not necessarily any less suitable than, say, the use of the boundary conditions specified at infinity that are often employed in ensemble averaging methods.

4. Analytical Solution for the Effective Dispersion Tensor

[15] Equation (19) can be solved directly for particular realizations of the velocity field and subsequently averaged to determine the unknown quantity $\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$ defining the macrodispersion. In Sec. 5 we will explore this approach

numerically using a Monte Carlo technique. Alternatively, for some velocity fields the statistics may be such that it is possible to develop an approximate analytical solution for $\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$, and here we will explore this latter approach. Our goal will be to show that the volume averaged solution for the time evolution of the effective dispersion tensor approaches the ensemble averaged result provided that: (1) the size of the averaging volume becomes sufficiently large, and (2) an assumption of ergodicity can be made that allows the equating of volume and ensemble averages. Although this result may seem at first to be expected, it is not necessarily an obvious one and we are aware of no other results that have made this correspondence directly for time-dependent effective parameters via volume averaging.

[16] To obtain an approximate analytical solution, we must introduce some simplifications to the closure problem. We begin by again making use of the decompositions for the velocity and dispersion tensor fields in order to express equation (22a) in the form

$$\frac{\partial\tilde{c}}{\partial t}+\langle\mathbf{v}\rangle\cdot\nabla\tilde{c}+\tilde{\mathbf{v}}\cdot\nabla\tilde{c}-\nabla\cdot(\langle\mathbf{D}\rangle\cdot\nabla\tilde{c})-\nabla\cdot(\tilde{\mathbf{D}}\cdot\nabla\tilde{c}) = -\tilde{\mathbf{v}}\cdot\nabla\langle c\rangle+\nabla\cdot\left(\tilde{\mathbf{D}}\cdot\nabla\langle c\rangle\right)+\nabla\cdot\langle\tilde{\mathbf{v}}\,\tilde{c}\rangle \tag{23}$$

Without making any approximations, we can rearrange the terms in this result to obtain

$$\frac{\partial\tilde{c}}{\partial t}+\langle\mathbf{v}\rangle\cdot\nabla\tilde{c}-\langle\mathbf{D}\rangle\cdot\nabla\nabla\tilde{c} = -\tilde{\mathbf{v}}\cdot\nabla\langle c\rangle+\left\{\nabla\cdot(\tilde{\mathbf{D}}\cdot\nabla\langle c\rangle)+\nabla\cdot(\tilde{\mathbf{D}}\cdot\nabla\tilde{c})+(\nabla\cdot\langle\mathbf{D}\rangle)\cdot(\nabla\tilde{c})+\nabla\cdot\langle\tilde{\mathbf{v}}\,\tilde{c}\rangle-\tilde{\mathbf{v}}\cdot\nabla\tilde{c}\right\} \tag{24}$$

The first four terms in this equation represent a linear form that can be solved analytically. In order to eliminate the remaining terms (in braces) we need to determine under what conditions they are negligible relative to the terms that are kept. This is examined in detail in section A3. Generally, it will be possible to neglect these terms under the conditions given by

$$L\gg\ell_{\mathrm{H}} \tag{25a}$$

$$\sigma_Y^2\ll 1 \tag{25b}$$

The first of these restrictions requires only that the characteristic length scale of the heterogeneities (e.g., the integral scale of the log conductivity field) is sufficiently small relative to the large length scale (which is generally much larger than the size of the averaging volume), and the second is the commonly adopted requirement that the variance of the normalized log conductivity field be sufficiently small. Note that these two conditions are required by nearly all perturbation theories (although often they are not explicitly identified as such) for obtaining expressions for the effective dispersion tensor in unconditioned fields. Adopting the restrictions given by equations (25), the closure problem takes the form

Simplified closure problem

$$\frac{\partial\tilde{c}}{\partial t}+\langle\mathbf{v}\rangle\cdot\nabla\tilde{c}-\langle\mathbf{D}\rangle:\nabla\nabla\tilde{c}=-\tilde{\mathbf{v}}\cdot\nabla\langle c\rangle \tag{26a}$$

Initial condition

$$\tilde{c}(\mathbf{x})=0\quad\text{at}\quad t=t_o \tag{26b}$$

Periodicity

$$\tilde{c}(\mathbf{x})=\tilde{c}(\mathbf{x}+\mathbf{l}_i) \tag{26c}$$

Averaging constraint

$$\langle\tilde{c}(\mathbf{x})\rangle=0 \tag{26d}$$

Note that these simplifications lead to a form for equation (26a) that is consistent with that of *Deng and Cushman* [1995a].

[17] Equations (26a)–(26d) can be solved using Fourier transform methods. It is important to note that because of periodicity, the deviation concentration field does not approach zero as $\mathbf{x}$ approaches infinity; therefore classical Fourier transform methods cannot be used for this problem. However, finite Fourier transform methods do exist for such periodic systems [e.g., *Churchill*, 1972]. A Fourier series solution for the perturbation concentration, $\tilde{c}$, in a periodic domain is developed in Appendix B using finite Fourier transform methods. Although the development in Appendix B is valid for nonstationary velocity fields, a solution for $\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle$ can be developed for a second-order spatially stationary random velocity field in terms of second-order statistics. The development follows much the same lines as that conducted by *Deng and Cushman* [1995a] who used an ensemble averaging technique in an infinite domain (like that work, the analysis can be put in a nonlocal form; in this work, however, we focus on the quasi-Fickian form also described by *Deng and Cushman* [1995a]). The result of our analysis (detailed in Appendix B) is

$$\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle=\left\{\frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')}\underline{\mathbf{R}}(\mathbf{k}')\right\}\cdot\nabla\langle c\rangle \tag{27}$$

where $\mathbf{k}'$ is a re-scaled Fourier coordinate

$$\mathbf{k}'=\frac{\mathbf{k}p}{\pi} \tag{28}$$

and $2p$ is the length of one side of the cube defining the unit cell. The spatially stationary velocity field covariance function and its transform are given by

$$\mathbf{R}(\mathbf{y})=\langle\tilde{\mathbf{v}}(\mathbf{y}+\mathbf{x})\tilde{\mathbf{v}}(\mathbf{x})\rangle \tag{29}$$

$$\underline{\mathbf{R}}(\mathbf{k}')=\int_{V(p)}\exp\left[-\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{y}\right]\mathbf{R}(\mathbf{y})dV_y \tag{30}$$

and the parameter $\beta(\mathbf{k}')$ is given by [cf. *Deng and Cushman*, 1995a]

$$\beta(\mathbf{k}')=\frac{i\pi}{p}\mathbf{k}'\cdot\langle\mathbf{v}\rangle+\frac{\pi^2}{p^2}\mathbf{k}'\cdot\langle\mathbf{D}\rangle\cdot\mathbf{k}' \tag{31}$$

Note that because we have a periodic system, the solution is specified in terms of a Fourier series rather than a Fourier integral.

[18] The closed-form of the macroscopic transport equation can be determined by substituting equation (27) into equation (17) to give

Macroscopic transport equation (closed form)

$$\frac{\partial \langle c \rangle}{\partial t} = -\langle \mathbf{v} \rangle \cdot \nabla \langle c \rangle + \nabla \cdot \left(\mathbf{D}_{eff} \cdot \nabla \langle c \rangle \right) \tag{32}$$

where the effective dispersion tensor is given by

Effective dispersion tensor (finite periodic unit cell)

$$\mathbf{D}_{eff}(t) = \langle \mathbf{D} \rangle + \frac{1}{(2p)^3} \sum_{k_3'=-\infty}^{k_3'=\infty} \sum_{k_2'=-\infty}^{k_2'=\infty} \sum_{k_1'=-\infty}^{k_1'=\infty} \frac{1 - \exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')} \underline{\mathbf{R}}(\mathbf{k}') \tag{33}$$

Equation (33) is a discrete Fourier series solution for the effective dispersion tensor, and as such it is ideally suited for solution via numerical methods. In principle, for any specified (discrete) velocity field over the unit cell, $\mathbf{D}_{eff}(t)$ can be determined by first determining the correlation function $\mathbf{R}(\mathbf{y})$ as defined by equation (29), next determining its (discrete) Fourier transform (equation (30)), and finally inverting as specified by equation (33). In practice, however, this may represent nearly the same effort as would be required to solve the differential equations for the deviations themselves using numerical methods. In Section 4 we will discuss the direct numerical approach in more detail.

[19] In order to maintain consistency with previously developed solutions [e.g., *Deng and Cushman*, 1995a; *Fiori and Dagan*, 2000], this result should converge to these results developed for infinite domains as the size of the averaging volume becomes increasingly large. Following the developments provided by *Wiener* [1933], it can be shown that the sum in equation (33) approaches an integral in the limit as the length scale p tends toward infinity; the result is

Effective dispersion tensor ($p \rightarrow \infty$)

$$\mathbf{D}_{eff}^{\infty}(t) = \langle \mathbf{D} \rangle + \frac{1}{(2\pi)^3} \int_{R^3} \frac{1 - \exp[-\beta(\mathbf{k})t]}{\beta(\mathbf{k})} \underline{\mathbf{R}}'(\mathbf{k}) d\mathbf{k} \tag{34}$$

When volume and ensemble averages are equivalent, this result is identical to the one obtained by *Deng and Cushman* [1995a] via ensemble averaging in an infinite domain. Note that this correspondence requires an assumption of ergodicity in the sense of *Cushman* [1983]. For second-order stationary velocity fields, equation (32) has been previously solved explicitly for $\mathbf{D}_{eff}^{\infty}(t)$ (or, equivalently, for the second moment of the solute plume) by *Deng et al.* [1993], *Deng and Cushman* [1995a], and by *Fiori and Dagan* [2000]. Note that both studies assumed a covariance function of the form described by *Gelhar and Axness* [1983].

[20] The solution provided by equation (34) is a useful endpoint for comparison with the effective dispersion tensor calculated in finite domains. In many instances, the assumptions that have been invoked to obtain the finite-domain solution given by equation (33) require more restrictions than we would like (e.g., the restrictions posed by equations (25a) and (25b)). In addition, we have no quantitative information about what size of averaging volume is "large enough" to assure that equation (34) represents a reasonably certain estimate of the effective dispersion tensor. To address these issues, we can solve the original closure problem, specified by equations (22a)–(22c), directly by numerical methods. Unlike ensemble averages, volume averages are well defined quantities for individual realizations of the hydraulic conductivity field. By generating many realizations of fields with the same underlying statistics for the conductivity field, Monte Carlo simulation can provide the information necessary to indicate how much variation in $\mathbf{D}_{eff}(t)$ there may be as a function of the size of the averaging volume. This information has practical significance in that it explains how much difference one could expect between the predicted value of the effective dispersion tensor, $\mathbf{D}_{eff}^{\infty}(t)$, obtained by assuming ergodicity, and the value of the realized effective dispersion tensor, $\mathbf{D}_{eff}(t)$, that might be measured in the field.

5. Numerical Solution for the Effective Dispersion Tensor

[21] As an alternative approach to the approximate analytical solution for the effective dispersion tensor, we can predict $\mathbf{D}_{eff}(t)$ exactly by numerical methods for individual realizations of the hydraulic conductivity field. There is a subtle but distinct difference between this approach and an approach that predicts the value of $\mathbf{D}_{eff}^{\infty}(t)$ versus one that predicts $\mathbf{D}_{eff}(t)$. One can predict for an individual realization of a velocity (or equivalently a hydraulic conductivity) field, even for finite-sized averaging volumes; however, this means that the spatial statistics that are calculated may not be equal to those of the ensemble (see discussions of this topic from the ensemble averaging perspective presented by *Dagan* [1991], *Rajaram and Gelhar* [1993], and *Christakos* [1992]). The result is that for each such realized field, the value of $\mathbf{D}_{eff}(t)$ that is calculated will vary somewhat from the ensemble average value given by $\mathbf{D}_{eff}^{\infty}(t)$. The term equivalent dispersion tensor (as distinct from effective dispersion tensor) has been used to describe the macrodispersion tensor computed for domains in which stationarity (and, hence, ergodicity) do not apply [e.g., *Renard and de Marsily*, 1997].

[22] Numerical solutions are one of the only means for determining equivalent parameters when the underlying conductivity fields are highly heterogeneous and not spatially stationary [e.g., *Durlofsky et al.*, 1994; *Pickup et al.*, 1994; *Ahmadi et al.*, 1998]. Even when the statistical structure of the velocity field is spatially stationary, numerical solutions may be advantageous because they allow one to obtain solutions with fewer approximations, or to examine domains that are not substantially larger than the characteristic length scale of the heterogeneities. A particular advantage of the numerical approach is that the velocity field can be determined exactly (to the accuracy of the numerical scheme), eliminating any questions regarding the use of first-order closure schemes for the flow field as done to obtain equations (33) and (34) (further discussion of this topic is given by *Deng and Cushman* [1995b, 1998]).

[23] One of the primary motivations for calculating the solution to the closure problem numerically is that it provides a direct method for answering the question "how large is large enough?" The ergodic hypothesis implies that volume and ensemble averages should become equivalent as the size of the averaging volume approaches infinite, but in practice, all measured statistics are of finite size. By conducting a Monte Carlo analysis of the closure problem for various sizes of unit cells, we can obtain information about how much variation there is in the volume averaged effective dispersion tensor, $\mathbf{D}_{eff}(t)$, as a function of unit cell size.

5.1. Numerical Closure Scheme

[24] We begin with equations (22a)–(22d), subject only to the assumption that the nonlocal term can be neglected (sections A1 and A2), i.e.,

$$\langle \mathbf{v} \rangle \cdot \nabla \tilde{c} \quad \gg \quad \nabla \cdot \langle \tilde{\mathbf{v}} \tilde{c} \rangle, \quad \text{when} \quad L \quad \gg \quad \ell_{\mathrm{H}} \tag{35}$$

Note that even though it is the quantity $\nabla \cdot \langle \tilde{\mathbf{v}} \tilde{c} \rangle$ that we wish to predict in order to close the macroscopic transport equation, this quantity can be neglected in the closure problem when the restriction given by equation (35) is met. The closure problem to be used in our numerical evaluation takes the form

$$\frac{\partial \tilde{c}}{\partial t} + \mathbf{v}(\mathbf{x}) \cdot \nabla \tilde{c} - \nabla \cdot (\mathbf{D}(\mathbf{x}) \cdot \nabla \tilde{c}) = -\tilde{\mathbf{v}}(\mathbf{x}) \cdot \nabla \langle c \rangle + \left(\nabla \cdot \tilde{\mathbf{D}}(\mathbf{x}) \right) \cdot (\nabla \langle c \rangle) \tag{36a}$$

Initial condition

$$\tilde{c}(\mathbf{x}) = 0 \quad \text{at} \quad t = t_{\mathrm{o}} \tag{36b}$$

Periodicity

$$\tilde{c}(\mathbf{x}) = \tilde{c}(\mathbf{x} + \mathbf{l}_i), \quad i = 1, 2, 3 \tag{36c}$$

Averaging constraint

$$\langle \tilde{c}(\mathbf{x}) \rangle = 0 \tag{36d}$$

At this point we note that the solution for $\tilde{c}$ can be expressed in the form [cf. *Quintard and Whitaker*, 1998b]

$$\tilde{c}(\mathbf{x}, t) = \mathbf{b}(\mathbf{x}, t) \cdot \nabla \langle c \rangle \tag{37}$$

The justification of this solution form can be found in equations (B30) and (B31) of Appendix B. Note that this assumes that we will obtain a quasi-Fickian [cf. *Deng and Cushman*, 1995a] form for the effective dispersion tensor. This is not a requirement of the volume averaging method, and nonlocal dispersion tensors can be obtained by volume averaging. Adopting this representation, equations (36a)–(36d) can be rewritten in the form

Closure problem (for numerical calculations)

$$\frac{\partial \mathbf{b}}{\partial t} + \mathbf{v}(\mathbf{x}) \cdot \nabla \mathbf{b} - \nabla \cdot (\mathbf{D}(\mathbf{x}) \cdot \nabla \mathbf{b}) = -\tilde{\mathbf{v}}(\mathbf{x}) + \nabla \cdot \tilde{\mathbf{D}}(\mathbf{x}) \tag{38a}$$

Initial condition

$$\mathbf{b}(\mathbf{x}, t_{\mathrm{o}}) = 0 \tag{38b}$$

Periodicity

$$\mathbf{b}(\mathbf{x}, t) = \mathbf{b}(\mathbf{x} + \mathbf{l}_i), \quad i = 1, 2, 3 \tag{38c}$$

Averaging constraint

$$\langle \mathbf{b}(\mathbf{x}, t) \rangle = 0 \tag{38d}$$

This form for the closure problem requires additionally that the following restriction be met

$$\mathbf{b} \cdot \frac{\partial (\nabla \langle c \rangle)}{\partial t} \quad \ll \quad \frac{\partial \mathbf{b}}{\partial t} \cdot \nabla \langle c \rangle \tag{39}$$

This restriction is based on the idea that the timescale associated with a change in the volume averaged concentration, $\langle c \rangle$, is much larger than the timescale for the spatial deviation concentration, $\tilde{c}$; the separation of timescales is discussed further in section A4. Note that equations (38a)–(38c) determine the **b**-field to within an arbitrary constant which is specified by the constraint on the average given by equation (36d).

5.2. Monte Carlo Simulations

[25] Equations (38a)–(38d) were solved numerically for an ensemble of 2-dimensional square periodic unit cells of increasing size. The underlying flow field was determined numerically by generating an ensemble of second-order stationary log conductivity field. Realizations of the log conductivity field were generated with the code HYDRO_GEN [*Bellin and Rubin*, 1996] using an exponential covariance model of the form

$$\langle Y'(\mathbf{x}) Y'(\mathbf{x}') \rangle_E \; = \; \sigma_Y^2 \cdot \exp\left\{ -\left[\frac{(\mathbf{x} - \mathbf{x}') \cdot (\mathbf{x} - \mathbf{x}')}{I_Y^2} \right]^{1/2} \right\} \tag{40}$$

where $\langle \ldots \rangle_E$ represents the expected (or ensemble or probabilistic) average [*Cushman*, 1983]. For the hydraulic conductivity, K, we use $Y = \ln K$ to define the variable Y, and Y_{o} is the ensemble mean value of Y. We use σ_Y^2 to represent the ensemble variance of Y, while $Y' = \ln K - Y_{\mathrm{o}}$ defines the deviation quantity that appears in equation (40). The integral scale, I_Y, is assumed to be isotropic and is defined by

$$I_Y = \int_{R^3} \langle Y'(\mathbf{x}) Y'(\mathbf{y}) \rangle_E d\mathbf{y} \tag{41}$$

This quantity is a constant because of the imposition of spatial stationarity.

[26] It is important to verify that the finite random fields that are generated actually do have the spatial statistics that are assumed. In particular, for this study, we want to be assured that the simulated fields meet the conditions of ergodicity; that is, that the ensemble statistics are equivalent to the spatial statistics as the size of the averaging volume tends toward infinity. The spatial covariance is given by the function

$$C_{xx}(\mathbf{x}, \mathbf{x}') \; = \; \langle Y'(\mathbf{x}) Y'(\mathbf{x}') \rangle = \frac{1}{V} \int_{\mathbf{x} \in \mathrm{V}} Y'(\mathbf{x}) Y'(\mathbf{x}') d\mathbf{x} \tag{42}$$

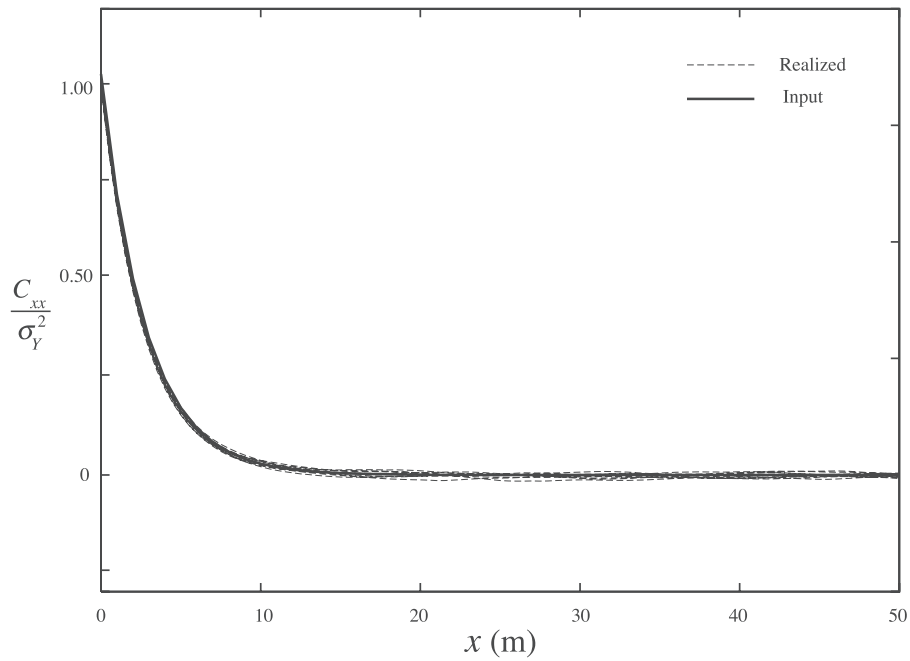

Figure 2. Examples showing convergence of the spatial and ensemble covariance functions of the conductivity fields for sufficiently large volumes (214 $I_Y \times$ 214 I_Y). Ten realizations of the conductivity field are represented.

In practice, it is not possible to verify the formal definition of ergodicity because the sampled points (whether simulated or measured) always represent a finite volume; therefore ergodicity is almost always a working hypothesis. However, from a practical standpoint, for second-order statistics one is generally satisfied to validate the following condition

$$\langle Y'(\mathbf{x})Y'(\mathbf{x}')\rangle_E \approx \lim_{\mathrm{V}\longrightarrow V_{REV}} \left(\frac{1}{V}\int_{\mathbf{x}\in\mathrm{V}} Y'(\mathbf{x})Y'(\mathbf{x}')d\mathbf{x}\right) \qquad (43)$$

where V_{REV} is a volume that is sufficiently large such that the two sides of this expression are "close enough" to be considered equal (in practice, "close enough" should be defined by a suitable metric that we will not pursue further here; see *Christakos* [1992, chap. 2] for additional details). In the literature, this concept is often referred to as "quasi-ergodicity" [e.g., *Christakos*, 1992]. The code used in this study [*Bellin and Rubin*, 1996] generates high-quality random fields that faithfully reproduce the input statistics in the sense of equation (43). To illustrate this correspondence, we have plotted C_{xx} (equation (42)) for 10 realizations of fields that are 214 $I_Y \times$ 214 I_Y (Figure 2). Figure 2 clearly illustrates that there is very little difference between the covariance function for each of these fields and the theoretical covariance given by equation (40). This provides strong evidence that the random field generator provides conductivity fields that are quasi-ergodic in the sense of equation (43).

[27] To investigate the influence of the size of the averaging volume, we calculated the effective dispersion tensor for square domains of 53.5, 107, and 214 integral scales (I_Y) in each dimension. The relative sizes and statistical structure of representative unit cells is illustrated in Figure 3. Each unit cell was discretized with a node spacing of 0.5 m in both directions; this resulted in unit cells that contained 300, 600, and 1200 nodes in each direction respectively. A number of realizations were generated for each unit cell size, with the constraint that the total number of computational nodes was constant.

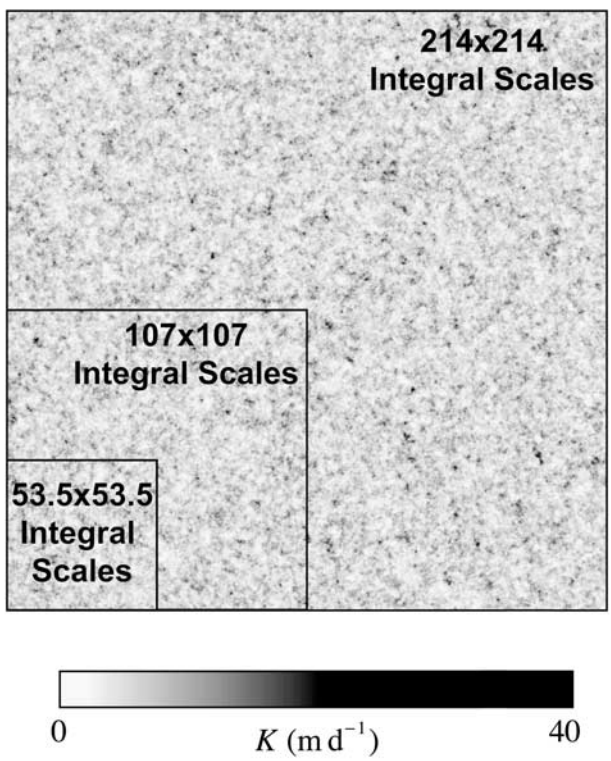

Figure 3. Examples of the three unit cell sizes used in this study.

Table 1. Parameters Used for Numerical Simulations of Dispersion in Periodic Unit Cells

Parameter	Value
D^*, m^2 d^{-1}	1.4×10^{-4}
I_{Yh}, m	2.8
K_G, m d^{-1}	6.18
$\langle v_1 \rangle$, m d^{-1}	0.09
$\langle v_2 \rangle$, m d^{-1}	0
α_L (Darcy scale), m	0.044
α_T (Darcy scale), m	0.0022
σ_Y^2	0.172
Δx, m	0.5
Δy, m	0.5
Δt, d	0.5

The following realizations were generated for the log conductivity field: 160 realizations of the 300 × 300 node case (case 1), 40 realizations of the 600 × 600 case (case 2), and 10 realizations of the 1200 × 1200 case (case 3) were generated for the log conductivity field.

[28] For each conductivity realization, the flow field was determined by specifying an averaged pressure gradient across the cell, imposing periodicity on the spatial velocity deviations, and imposing no flow conditions on the faces parallel to the direction of the averaged pressure gradient. This scheme leads to a volume averaged velocity field (where the averaging volume is taken to be the size of one unit cell in the periodic domain) that is constant in the x direction, and zero in the y direction. Relevant parameters for the numerical analysis are summarized in Table 1. Note that we have used the definition $K_G = \exp(Y_o)$ in this tabulation. The flow field was computed using a standard finite-volume formulation of the flow equation over a Cartesian regular mesh.

[29] For the transport problem, the equations were split in separate convective and dispersive terms, and then solved sequentially. The boundary conditions were the periodic condition specified by equation (38c) using equation (38d) as a constraint. Each realization was simulated for a time period of 1200 days (in terms of dimensionless time, $\langle v_x \rangle t/I_Y = 38.6$) with a time step of 0.5 days. For case 1, only the first (approximately) 600 days of the solution are shown because of artifacts that are generated if the motion due to mean convection traverses distances greater than the size of the domain (if the convective motion is followed for a time greater than the time required to traverse the unit cell, the same features of the velocity field will be re-sampled, leading to spurious long-range correlations). An explicit TVD scheme is implemented to solve the convective term [*Harten*, 1983; *Tackacs*, 1985]. The scheme is second-order when the concentration field is smooth, and reduces to first-order near sharp fronts. The Darcy-scale dispersion was assumed dependent upon the velocity field as described by *Bear* [1961], and this formulation leads to a full Darcy-scale dispersion tensor of the form

$$D_{ij}(x) = D^*\delta_{ij} + \alpha_T||\mathbf{v}||\delta_{ij} + (\alpha_L - \alpha_T)v_i v_j/||\mathbf{v}|| \qquad (44)$$

where D^* is the diffusion coefficient, and α_L and α_T are the lateral and transverse dispersivity, respectively. Accurate representation of the diffusive term requires 9-cell support in two dimensions. We used a flux continuous, locally conservative implicit finite volume method for obtaining the solution to the dispersion problem. This scheme is a modification of that proposed by *Edwards and Rogers* [1994] for full permeability tensors [*Cherblanc et al.*, 2003]. This net result is a second order scheme for the solute transport with negligible numerical dispersion. For the numerical simulations, convergence analyses were conducted to assure that the scheme was providing solutions free from excessive numerical dispersion.

5.3. Effective Dispersion Tensor for a Single Unit Cell Realization

[30] The effective dispersion tensor was determined for each realization by multiplying the solution for the deviation concentration by the deviation velocity for each point on the discretized unit cell. This result was then averaged over the volume to provide a direct calculation of the quantity

$$\langle \tilde{\mathbf{v}}(\mathbf{x})\tilde{c}(\mathbf{x},t)\rangle = \langle \tilde{\mathbf{v}}(\mathbf{x})\mathbf{b}(\mathbf{x},t)\rangle \cdot \nabla\langle c\rangle \qquad (45)$$

Finally, substituting this result into the macroscopic transport equation (equation (17)) yields a definition for the effective dispersion tensor that is analogous to that developed from the analytical approach

$$\mathbf{D}_{eff} = \langle \mathbf{D}\rangle + \langle \tilde{\mathbf{v}}(\mathbf{x})\mathbf{b}(\mathbf{x},t)\rangle \qquad (46)$$

Results from the numerical calculations of the effective dispersion tensor for three sizes of unit cells are given in Figures 4 and 5. In Figure 4 we have illustrated representative plots of the effective dispersion tensor as a function of time for multiple realizations (only the first 20 realizations are shown for case 1, and only the first 10 realizations are shown for case 2; all realizations are shown for case 3). The primary feature to be observed here is that for small unit cells (case 1, 53.5 I_Y × 53.5 I_Y) the effective dispersion tensor has significant variation, and is not necessarily even monotonic. Although it is not surprising to expect the effective dispersion tensor to be a function of the size of the averaging volume, it was somewhat unexpected to find that unit cells that were more than 50 integral scales per side still exhibited significant fluctuations in the effective dispersion tensor. Similar predictions have been made by *Dagan* [1990] and by *Fiori* [1998] for the asymptotic value of the variance of D_{11}.

5.4. Statistics of the Effective Dispersion Tensor Over Realizations of the Unit Cell

[31] In the subsequent discussion, we will make use of some statistics of the volume averaged dispersion tensor. We define the following statistical measures for the ensemble of unit cell realizations. Average

$$\bar{\mathsf{D}}_{eff,11}(t) = \frac{1}{N}\sum_{i=1}^{i=N} \mathsf{D}^i_{eff,11}(t) \qquad (47a)$$

$$\bar{\mathsf{D}}_{eff,22}(t) = \frac{1}{N}\sum_{i=1}^{i=N} \mathsf{D}^i_{eff,22}(t) \qquad (47b)$$

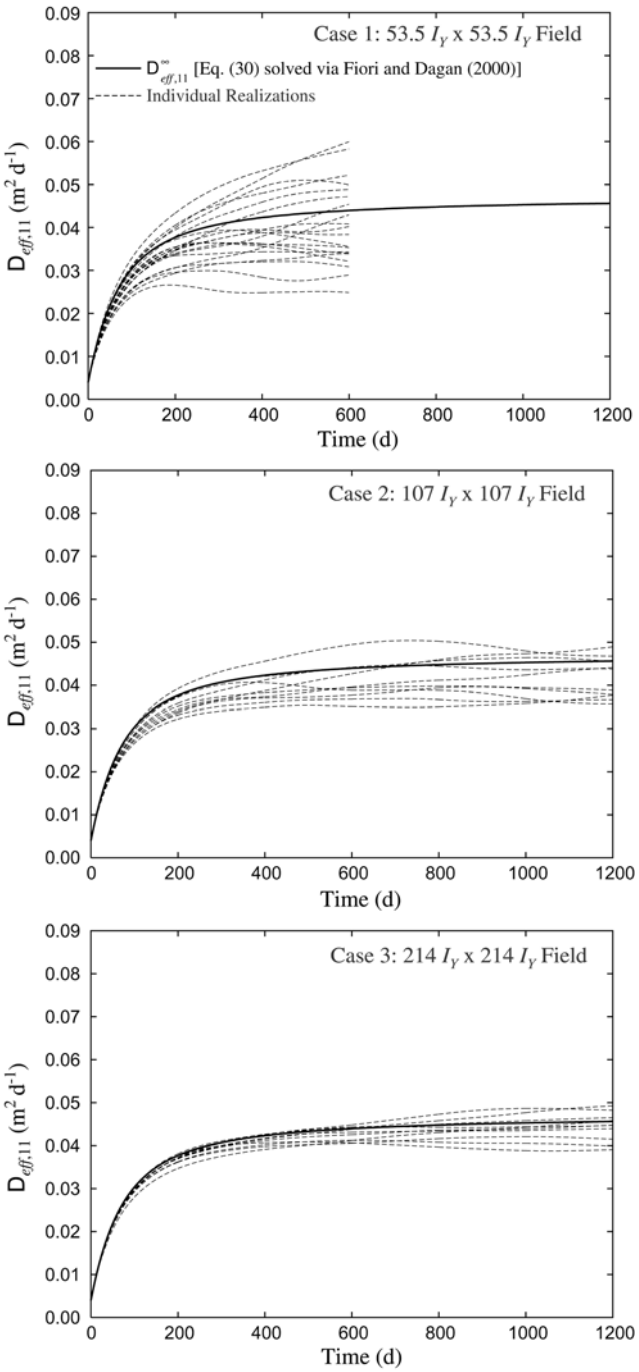

Figure 4. Realizations of the effective dispersion tensor component D_{11} for the three unit cell sizes.

Variance

$$\sigma^2_{D,11}(t) = \frac{1}{N-1}\sum_{i=1}^{i=N}\left[\mathsf{D}^i_{eff,11}(t) - \bar{\mathsf{D}}_{eff,11}(t)\right]^2 \tag{48a}$$

$$\sigma^2_{D,22}(t) = \frac{1}{N-1}\sum_{i=1}^{i=N}\left[\mathsf{D}^i_{eff,22}(t) - \bar{\mathsf{D}}_{eff,22}(t)\right]^2 \tag{48b}$$

Coefficient of variation

$$CV_{D,11}(t) = \frac{\sigma_{D,11}(t)}{\bar{\mathsf{D}}_{eff,11}(t)} \tag{49a}$$

$$CV_{D,22}(t) = \frac{\sigma_{D,22}(t)}{\bar{\mathsf{D}}_{eff,22}(t)} \tag{49b}$$

where N is the number of realizations of the unit cell, a superscript i indicates the *ith* realization, where the overbar indicates the average over an ensemble of realizations of the unit cell. Note that because of the finite size of the unit cell, the average defined above is slightly different than the ensemble average, which is typically taken over an ensemble of infinite velocity field domains.

[32] The variance of the effective dispersion tensor can also be calculated directly from equation (33). To begin, note that for any unit cell, we have from equation (33)

$$\bar{\mathbf{D}}_{eff}(t) = \langle \mathbf{D} \rangle + \frac{1}{(2p)^3}\sum_{k'_3=-\infty}^{k'_3=\infty}\sum_{k'_2=-\infty}^{k'_2=\infty}\sum_{k'_1=-\infty}^{k'_1=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')}\overline{\mathbf{R}}(\mathbf{k}') \tag{50}$$

Using this definition and equation (33), the variance of the effective dispersion tensor (which is itself a tensor) takes the form

$$\boldsymbol{\sigma}^2_D = \frac{1}{N-1}\sum_{i=N}^{i=1}\left[\mathbf{D}^i_{eff}(t) - \overline{\mathbf{D}}_{eff}(t)\right]\cdot\left[\mathbf{D}^i_{eff}(t) - \overline{\mathbf{D}}_{eff}(t)\right] \tag{51}$$

where as before a superscript i indicates the *ith* realization. Although equation (51) is a Fourier series solution for the variance of the effective dispersion tensor, it is not necessarily any more convenient to work with this series directly than it is to work with a differential equation for $\tilde{c}$ which can ultimately be used to determine the variance through equations (47a) and (47b). Therefore the Monte Carlo solutions to the closure problem (equations (38a)–(38c)) described above provide an effective means of calculating the variance tensor components $\sigma^2_{D,11}$ and $\sigma^2_{D,22}$.

6. Results and Discussion

[33] In Figure 5 we have plotted the average value (equations (47a) and (47b)) and the coefficient of variation (equations (49a) and (49b)) of the effective dispersion tensor for each of the three unit cell sizes. The values of the diagonal components of the average dispersion tensor have been indicated by $\overline{\mathsf{D}}_{eff,11}$ and $\overline{\mathsf{D}}_{eff,22}$. The components of the infinite domain effective dispersion tensor, $\mathbf{D}^{\infty}_{eff}$, predicted by equation (34) (adopting the analytical solution presented by *Fiori and Dagan* [2000]) and the variance of the effective dispersion tensor (using an updated version of the analytical solution developed by *Fiori* [1998], detailed in Appendix C) are also plotted for comparison. Two trends are evident in Figure 5: (1) as the size of the averaging volume increases, the variation in the effective dispersion tensor components decreases and its mean value approaches $\mathbf{D}^{\infty}_{eff}$, and (2) the uncertainty in the effective dispersion tensor components generally increases in time.

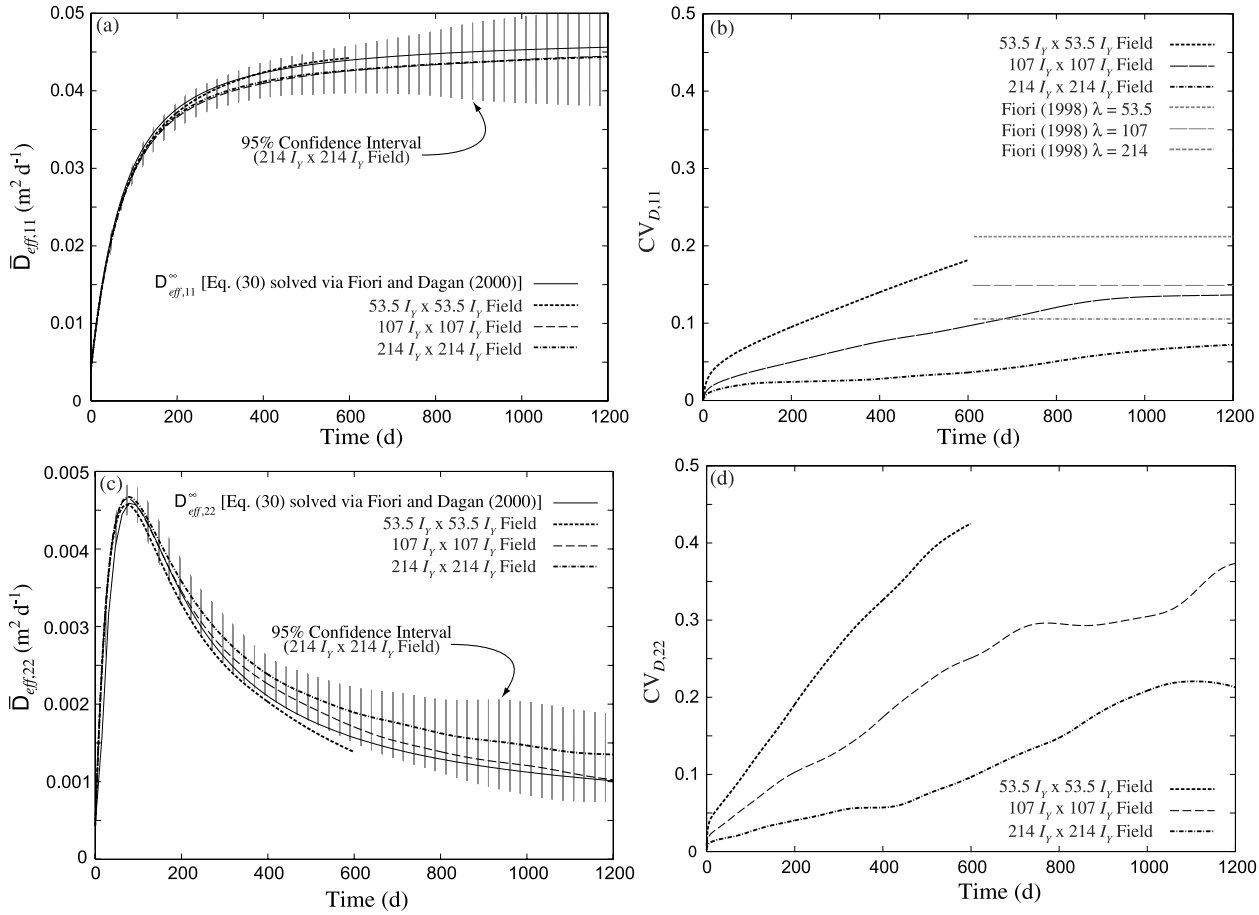

Figure 5. Comparisons of the Monte Carlo averages and coefficient of variation for the effective dispersion tensor with the analytical expressions of *Fiori* [1998] (with revisions described in Appendix C of this work) and *Fiori and Dagan* [2000].

[34] In regard to the first trend, Figures 5b and 5d show how the coefficient of variation decreases as a function of the size of the unit cell. As the unit cell becomes larger, the variation in the effective diffusion tensor decreases. Despite the clear differences in $CV_{D,11}$ and $CV_{D,22}$ for the three averaging volume sizes, it is interesting to note that the mean values $\overline{\mathsf{D}}_{eff,11}$ and $\overline{\mathsf{D}}_{eff,22}$ were similar for the three cases considered. In Figures 5a and 5c we have indicated by vertical lines the 95% confidence interval for $\overline{\mathsf{D}}_{eff,11}$ and $\overline{\mathsf{D}}_{eff,22}$ for the largest (214 $I_Y \times$ 214 I_Y) unit cell. The largest unit cell generates realizations for the effective dispersion tensor with the smallest variance, and hence it has the narrowest confidence interval among the three cases. Nonetheless, with the exception of $\overline{\mathsf{D}}_{eff,22}$ for case 1 (53.5 $I_Y \times$ 53.5 I_Y), the values for $\overline{\mathsf{D}}_{eff,11}$ and $\overline{\mathsf{D}}_{eff,22}$ for all cases were within this confidence interval. The results presented in Figure 4 suggest that there were sufficient realizations for each of the three cases considered such that values for $\overline{\mathsf{D}}_{eff,11}$ and $\overline{\mathsf{D}}_{eff,22}$ were statistically indistinguishable from one another with a high degree of confidence.

[35] The cause of the second trend noted above (i.e., the increasing uncertainty in the effective dispersion tensor with increasing time) is somewhat less intuitive than the first. The reason for this second trend becomes clearer by examining the individual realizations of $\overline{\mathsf{D}}_{eff,11}$ that are plotted in Figure 4. As the size of the averaging volume decreases, there is an increasing probability of obtaining an effective dispersion tensor that deviates significantly from the average. Because all realizations have identical initial conditions, the variance in the dispersion tensor is necessarily zero at the initial time. As time increases, however, the effect of a dispersion tensor that deviates significantly from the mean becomes substantially more pronounced, causing an increasing value for the coefficient of variation with increasing time. The solution developed by *Fiori* [1998] (see also Appendix C of this work) provides the asymptotic value of the variance of the dispersion tensor for the case of an infinite Péclet number. Our numerical results are consistent with those analytical solutions, both in magnitude and in the trend toward an asymptotic value (although the presence of a nonzero local dispersion may alter the approach to an asymptote for the long-time solution, the asymptotic solution with $Pe = 0$ is reasonable in any case for $tD_{11}/I_Y^2 \ll 1$ (A. Fiori, personal communication).

[36] These results suggest that even for large (relative to the integral scale) domains, there may be significant variability in the value of $\mathbf{D}_{eff}$ for any particular realization. This observation has some significant ramifications. Although equation (34) can be used to generate accurate estimates of $\overline{\mathbf{D}}_{eff}$, it does not provide any indication as to how much variation there might be between this averaged value and any

value, $\mathbf{D}_{eff}$, that is actually realized. The Monte Carlo analysis for the variation in $\mathbf{D}_{eff}$ suggest that (1) increasing the size of the unit cell decreases the variation in $\mathbf{D}_{eff}$ and (2) the variation of $\mathbf{D}_{eff}$ appears to (asymptotically) increase with increasing time. Therefore the confidence that one has in a particular value for the effective dispersion tensor is a function of both the size of the unit cell and of the total observation time. For t less than about 100 days ($\langle v_x \rangle t/I_Y < 3$) each of the three unit cell sizes provided estimates for $\mathbf{D}_{eff}$ that were close to the mean (the coefficient of variation was less than 0.1). However, only the largest (214 $I_Y \times$ 214 I_Y) unit cell provided a high degree of certainty in the asymptotic value of $\mathbf{D}_{eff}$ ($CV_{D,11} < 0.1$ and $CV_{D,22} < 0.25$). Two important additional points need to be made in regard to these results. The first is that these results are for 2-dimensional systems; the extra degree of freedom that occurs in an equivalent three-dimensional system may reduce the variance in $\mathbf{D}_{eff}$ that is observed. Secondly, this analysis does not account for the possibility of conditioning conductivity data on measured values. Although such conditioning would be expected to reduce the variability of the realized values for $\mathbf{D}_{eff}$, such an analysis is beyond the scope of this paper.

7. Summary and Conclusions

[37] In this paper we have established a representation for the effective dispersion tensor using the method of volume averaging and adopting a periodic unit cell for solution to the closure problem. In addition, we have examined the effect that the size of the unit cell (or averaging volume) has upon the determination of the effective dispersion tensor. Our main results can be summarized as follows.

[38] 1. A Fourier series representation can be developed for the effective dispersion tensor in a finite volume with periodic boundaries. In principle, this solution can be evaluated under relatively general conditions using numerical Fourier transform and inversion methods. For a second-order stationary log conductivity field, as the period of the unit cell becomes infinite, the solution approaches the quasi-Fickian solution developed previously by *Deng and Cushman* [1995a] and the Lagrangian solution recently reported by *Fiori and Dagan* [2000]. Similar correspondence between Eulerian and Lagrangian approaches have been previously illustrated by *Cushman et al.* [1996] for the case where local dispersion is neglected.

[39] 2. The numerical results establish that each of the unit cells sizes considered yields a values for the average effective dispersion tensor, $\overline{\mathbf{D}}_{eff}$, that converges (within a 95% confidence interval) to the dispersion tensor obtained for an infinite domain, $\mathbf{D}_{eff}^{\infty}$. These results are consistent with those obtained by *Rubin et al.* [1999], who examined sub-grid-scale dispersion from an ensemble averaging approach. This suggests that the limiting integral solution given by equation (34) provides a good estimate of the average effective dispersion tensor, $\overline{\mathbf{D}}_{eff}$, that would be obtained for an ensemble of unit cells that are at least 50 $I_Y \times$ 50 I_Y in size or larger. Note that we have not calculated the effective dispersion tensor that is obtained via volume averaging for unit cells smaller than this size. Results from *Rubin et al.* [1999, Figures 3 and 4] and *Fiori* [1998, Figure 4] suggest that for unit cells smaller than 50 $I_Y \times$ 50 I_Y, equation (34) will not provide a reasonable estimate for the effective dispersion tensor. However, for such situations the numerical procedure described in section 5 can still provide an estimate of $\mathbf{D}_{eff}$ for any particular realization or ensemble of realizations. In three-dimensional systems the uncertainty in $\mathbf{D}_{eff}$ may be reduced (for an equivalent characteristic length) from that observed in two dimensions because of the extra degree of freedom; a three-dimensional analysis along the lines of this study should be completed to better understand the variation of the effective dispersion tensor in three-dimensional systems.

[40] 3. Although the average value, $\overline{\mathbf{D}}_{eff}$, can be accurately estimated by an ensemble of unit cells (even for the smallest cells studied), the actual value of the dispersion tensor determined for any one realization, $\mathbf{D}_{eff}$, can show significant variations from the mean value. These variations increased with time (as illustrated in Figures 5b and 5d). Even for the largest unit cell (214 $I_Y \times$ 214 I_Y) the coefficient of variation for the largest times simulated in this study (1200 days or $\langle v_x \rangle t/I_Y = 38.6$) was less than 0.1 for $D_{eff,11}$ and just over 0.2 for $D_{eff,22}$. A Fourier series solution for the variance of the effective dispersion tensor can be developed, and is presented as equation (51). In practice, however, it may be no more convenient to use this solution than it is to solve the closure problem directly. In either case, a numerical solution is required to determine the variance of $\mathbf{D}_{eff}$ as a function of the size of the unit cell. The analytical solution developed by *Fiori* [1998] (with corrections and revisions provided by A. Fiori in Appendix C of this work) is a robust estimate of the asymptotic value of the variance of D_{11} for many practical conditions.

[41] 4. The analysis presented here assumes a priori that the macroscopic transport equation will honor only the first two moments of the concentration field. Although not described in detail here, it is possible to extend the Eulerian volume averaging approach to provide a transport equation that faithfully represents the higher-order moments of the mean concentration field. Under some conditions (e.g., reactive transport) higher-order moments may be critical for understanding the plume evolution. However, the calculation of higher-order moments should be adopted cautiously because in practice the ability to accurately measure these moments may be difficult. The development of transport equations with higher-order derivatives is an area for continuing research.

Appendix A: Length-Scale Constraints

[42] In this appendix we consider the simplification of various terms that appear in the volume averaged transport equation and the closure problem.

A1. Average of Average Quantities

[43] Unlike the case for ensemble averages, the volume average of an average quantity does not recover the average identically. Instead, this is true only as an approximation for suitably posed random fields. To determine the conditions for which this approximation is valid, we begin by considering the average of a volume averaged quantity, $\langle \psi \rangle$, which we express explicitly as

$$\langle \langle \psi \rangle \rangle|_{\mathbf{x}} = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \langle \psi \rangle|_{\mathbf{x}+\mathbf{y}} dV \tag{A1}$$

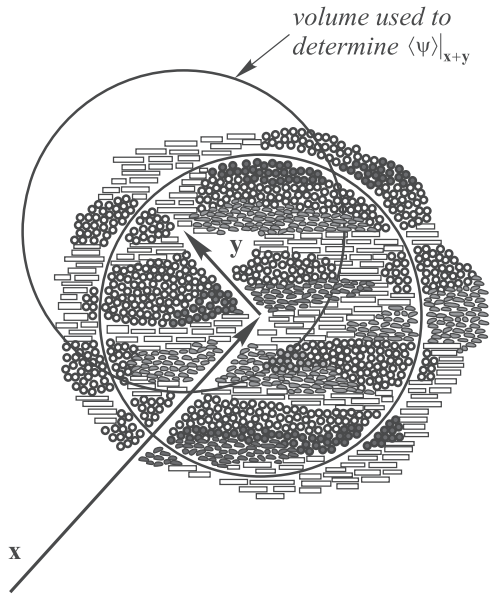

Figure A1. Position vectors associated with an averaging volume.

Here **x** locates the centroid of the averaging volume and **y** is the relative position vector as shown in Figure A1. The integrand in equation (A1) is associated with the position **x** + **y**, thus the length associated with the integral is $4R_o$ rather than $2R_o$ where R_o is the radius of the averaging volume. A Taylor series expansion about the centroid of the averaging volume leads to

$$\langle\psi\rangle|_{\mathbf{x}+\mathbf{y}} = \langle\psi\rangle|_{\mathbf{x}} + \mathbf{y}\cdot\nabla\langle\psi\rangle|_{\mathbf{x}} + \mathbf{yy}:\nabla\nabla\langle\psi\rangle|_{\mathbf{x}} + \ldots \tag{A2}$$

and when this result is used in equation (A1) we have

$$\langle\langle\psi\rangle\rangle|_{\mathbf{x}+\mathbf{y}} = \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\langle\psi\rangle|_{\mathbf{x}}dV + \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\mathbf{y}\cdot\nabla\langle\psi\rangle|_{\mathbf{x}}dV + \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\mathbf{yy}:\nabla\nabla\langle\psi\rangle|_{\mathbf{x}}dV + \ldots \tag{A3}$$

The quantities evaluated at **x** can be removed from the integrals to obtain

$$\langle\langle\psi\rangle\rangle|_{\mathbf{x}+\mathbf{y}} = \langle\psi\rangle|_{\mathbf{x}} + \langle\mathbf{y}\rangle\cdot\nabla\langle\psi\rangle|_{\mathbf{x}} + \langle\mathbf{yy}\rangle:\nabla\nabla\langle\psi\rangle|_{\mathbf{x}} + \ldots \tag{A4}$$

and evaluation of the spatial moments of **y** leads to [*Whitaker*, 1999, chap. 1]

$$\langle\mathbf{y}\rangle = 0, \qquad \langle\mathbf{yy}\rangle = O\left(\frac{R_o^2}{5}\right) \tag{A5}$$

Use of these results in equation (A4) provides

$$\langle\langle\psi\rangle\rangle|_{\mathbf{x}+\mathbf{y}} = \langle\psi\rangle|_{\mathbf{x}} + O\left(\frac{R_o^2}{5}\nabla\nabla\langle\psi\rangle|_{\mathbf{x}}\right) + \ldots \tag{A6}$$

We can estimate $\nabla\nabla\langle\psi\rangle$ according to

$$\nabla\nabla\langle\psi\rangle = O\left(\frac{\nabla\langle\psi\rangle}{L^2}\right) \tag{A7}$$

Here L is the characteristic length associated with variations in $\langle\{\psi\}\rangle$ (see Figure 1), and use of this result in equation (A6) leads to

$$\langle\langle\psi\rangle\rangle|_{\mathbf{x}} = \langle\psi\rangle|_{\mathbf{x}} + O\left[(R_o/L)^2\nabla\langle\psi\rangle\right] \tag{A8}$$

When the following constraint is imposed

$$(R_o/L)^2 \ll 1 \tag{A9}$$

we see that equation (A8) simplifies to

$$\langle\langle\psi\rangle\rangle|_{\mathbf{x}} = \langle\psi\rangle|_{\mathbf{x}} \tag{A10}$$

[44] Using this result, one can take the average of the spatial decomposition

$$\langle\psi\rangle = \langle\langle\psi\rangle\rangle + \langle\tilde{\psi}\rangle \tag{A11}$$

to conclude that

$$\langle\tilde{\psi}\rangle = 0 \tag{A12}$$

whenever the constraint given by equation (A9) is valid.

A2. Average of Products

[45] The use of equation (A10) allows us to simplify equation (8) to equation (11); however, the restrictions illustrated by equation (12) are associated with a product of the type, $\langle\tilde{S}\langle\psi\rangle\rangle$, in which S is a spatial deviation quantity. To be explicit, we represent this average of a product according to

$$\langle\tilde{S}\langle\psi\rangle\rangle|_{\mathbf{x}} = \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\langle\psi\rangle|_{\mathbf{x}+\mathbf{y}}dV \tag{A13}$$

and use of the Taylor series expansion given by equation (A2) to obtain

$$\langle\tilde{S}\langle\psi\rangle\rangle|_{\mathbf{x}} = \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\langle\psi\rangle|_{\mathbf{x}}dV + \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}\cdot\nabla\langle\psi\rangle|_{\mathbf{x}}dV + \frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{yy}\cdot\nabla\nabla\langle\psi\rangle|_{\mathbf{x}}dV + \ldots \tag{A14}$$

At this point we can make use of equation (A10) to remove the average quantities evaluated at **x** from the volume integral in order to obtain

$$\langle\tilde{S}\langle\psi\rangle\rangle|_{\mathbf{x}} = \left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}dV\right\}\langle\psi\rangle|_{\mathbf{x}} + \left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}dV\right\}\cdot\nabla\langle\psi\rangle|_{\mathbf{x}} + \left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{yy}dV\right\}\cdot\nabla\nabla\langle\psi\rangle|_{\mathbf{x}} + \ldots \tag{A15}$$

Whenever equation (A10) is valid, we can make use of equation (A12) to obtain

$$\left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}dV\right\}=0 \tag{A16}$$

and equation (A15) simplifies to

$$\langle\tilde{S}\langle\psi\rangle\rangle\big|_{\mathbf{x}}=\left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}dV\right\}\cdot\nabla\langle\psi\rangle\big|_{\mathbf{x}}+\left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}\mathbf{y}dV\right\}:\nabla\nabla\langle\psi\rangle\big|_{\mathbf{x}}+\ldots \tag{A17}$$

If the spatial deviation, S, were spatially stationary we could argue that

$$\left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}dV\right\}=0 \tag{A18}$$

as the averaging volume became large enough. This would allow us to simplify equation (A17) to the form

$$\langle\tilde{S}\langle\psi\rangle\rangle\big|_{\mathbf{x}}=\left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}\mathbf{y}dV\right\}:\nabla\nabla\langle\psi\rangle\big|_{\mathbf{x}}+\ldots \tag{A19}$$

A severe overestimate of the term in braces would be

$$\left\{\frac{1}{\mathcal{V}}\int_{\mathcal{V}}\tilde{S}\mathbf{y}\mathbf{y}dV\right\}=\mathsf{O}\left(\tilde{S}R_{\mathrm{o}}^2\right) \tag{A20}$$

Use of this result along with the estimate of the second derivative

$$\nabla\nabla\langle\psi\rangle\big|_{\mathbf{x}}=\mathsf{O}\left(\nabla\langle\psi\rangle/L^2\right) \tag{A21}$$

leads to

$$\langle\tilde{S}\langle\psi\rangle\rangle\big|_{\mathbf{x}}=\mathsf{O}\left(\tilde{S}\langle\psi\rangle R_{\mathrm{o}}^2/L^2\right) \tag{A22}$$

Use of this type of estimate with equations (12) leads to

$$\langle\langle\mathbf{v}(\mathbf{x})\rangle\tilde{c}\rangle=\mathsf{O}\left(\langle\mathbf{v}(\mathbf{x})\rangle\tilde{c}R_{\mathrm{o}}^2/L^2\right)\ll\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle \tag{A23}$$

$$\langle\tilde{\mathbf{v}}(\mathbf{x})\langle\tilde{c}\rangle\rangle=\mathsf{O}\left(\tilde{\mathbf{v}}(\mathbf{x})cR_{\mathrm{o}}^2/L^2\right)\ll\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle \tag{A24}$$

These two results are certainly appealing restrictions and motivate the replacement of equation (11) with equation (13) whenever the inequality given by equation (9) is valid. However, estimating the terms in equation (11) is difficult and the validity of equation (13) remains as an open question. A similar situation exits for the analysis of the classic Darcy-scale dispersive transport [*Whitaker*, 1999, Sec. 3.2.3].

[46] In addition to the simplifications indicated by equations (A23) and (A24), our development of the volume averaged equation given by equation (17) required the restriction

$$\nabla\cdot\langle\mathbf{D}(\mathbf{x})\cdot\nabla\tilde{c}\rangle\quad\ll\quad\nabla\cdot\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle \tag{A25}$$

When equation (A10) is valid, we can decompose the dispersion tensor to obtain

$$\begin{aligned}\langle\mathbf{D}(\mathbf{x})\cdot\nabla\tilde{c}\rangle&=\langle\langle\mathbf{D}\rangle\cdot\nabla\tilde{c}+\tilde{\mathbf{D}}\cdot\nabla\tilde{c}\rangle=\langle\mathbf{D}\rangle\cdot\langle\nabla\tilde{c}\rangle+\langle\tilde{\mathbf{D}}\cdot\nabla\tilde{c}\rangle\\&=\langle\tilde{\mathbf{D}}\cdot\nabla\tilde{c}\rangle\end{aligned} \tag{A26}$$

and the inequality given by equation (A25) takes the form

$$\langle\tilde{\mathbf{D}}(\mathbf{x})\cdot\nabla\tilde{c}\rangle\ll\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle \tag{A27}$$

Our estimate of $\nabla\tilde{c}$ takes the form,

$$\nabla\tilde{c}=\mathsf{O}(\tilde{c}/\ell_{\mathrm{H}}) \tag{A28}$$

where ℓ_{H} is the length scale associated with the heterogeneities illustrated in Figure 1, and if one is willing to estimate the right hand side of equation (A27) according to

$$\langle\tilde{\mathbf{v}}(\mathbf{x})\tilde{c}\rangle=\mathsf{O}(\langle\mathrm{v}\rangle\tilde{c}) \tag{A29}$$

the restriction given by equation (A27) can be arranged in the form

$$\langle Pe\rangle\gg\tilde{\mathsf{D}}/\mathsf{D} \tag{A30}$$

Here $\langle Pe\rangle$ represents an average Péclet number defined by

$$\langle Pe\rangle=\frac{\langle\mathrm{v}\rangle\ell_{\mathrm{H}}}{\mathsf{D}} \tag{A31}$$

while D and $\tilde{\mathsf{D}}$ represent suitable norms for both $\mathbf{D}$ and $\tilde{\mathbf{D}}$. One must keep in mind that estimates associated with vectors and tensors are less accurate than one would like, and detailed calculations associated with the inequality given by equation (A25) are certainly in order.

A3. Velocity Perturbation Terms

[47] We begin by noting that

$$\langle\mathbf{v}\rangle\cdot\nabla\tilde{c}\ \gg\ \nabla\cdot\langle\tilde{\mathbf{v}}\tilde{c}\rangle,\quad\text{when } L\ \gg\ \ell_{\mathrm{H}} \tag{A32}$$

$$\langle\mathbf{D}\rangle:\nabla\nabla\tilde{c}\ \gg\ (\nabla\cdot\langle\mathbf{D}\rangle)\cdot(\nabla\tilde{c}),\text{when}\ \ L\ \gg\ \ell_{\mathrm{H}} \tag{A33}$$

Here the characteristic length scale associated with spatial deviation quantities, such as $\tilde{c}$, is the small length scale, ℓ_{H}. These length scales are illustrated in Figure 1, and the constraint, $L\gg\ell_{\mathrm{H}}$, is a reasonable one for many subsurface systems. The use of equations (A32) and (A33) allows us to simplify equation (24) to the form

$$\begin{aligned}\frac{\partial\tilde{c}}{\partial t}+\langle\mathbf{v}\rangle\cdot\nabla\tilde{c}-\langle\mathbf{D}\rangle:\nabla\nabla\tilde{c}&=-\tilde{\mathbf{v}}\nabla\langle c\rangle\\&+\left\{\nabla\cdot\left(\tilde{\mathbf{D}}\cdot\nabla\langle c\rangle\right)+\nabla\cdot\left(\tilde{\mathbf{D}}\cdot\nabla\tilde{c}\right)-\tilde{\mathbf{v}}\cdot\nabla\tilde{c}\right\}\end{aligned} \tag{A34}$$

[48] There remain three terms which we would like to discard, but it is difficult to develop constraints indicating the conditions for which these terms can be neglected. Since

both $\tilde{\mathbf{D}}$ and $\tilde{c}$ have the same length scale, it is a straightforward matter to construct the estimate

$$\nabla \cdot \left(\tilde{\mathbf{D}} \cdot \nabla \tilde{c}\right) = \mathrm{O}\left(\tilde{\mathrm{D}}\tilde{c}/\ell_{\mathrm{H}}^2\right) \tag{A35}$$

which leads to

$$\langle \mathbf{D} \rangle : \nabla\nabla\tilde{c} \gg \nabla \cdot \left(\tilde{\mathbf{D}} \cdot \nabla \tilde{c}\right), \quad \text{when } \langle \mathrm{D} \rangle \gg \tilde{\mathrm{D}} \tag{A36}$$

Under many circumstances, it might be necessary to assume that $\tilde{\mathbf{D}} \approx \langle \mathbf{D} \rangle$. However, when the velocity field variance is sufficiently small relative to the mean, i.e.,

$$\sigma_Y^2 \ll 1 \tag{A37}$$

we would expect that $\tilde{\mathbf{D}} \ll \langle \mathbf{D} \rangle$. Discarding $\nabla \cdot (\tilde{\mathbf{D}} \cdot \nabla \tilde{c})$, we see that equation (A34) takes the form

$$\frac{\partial \tilde{c}}{\partial t} + \langle \mathbf{v} \rangle \cdot \nabla \tilde{c} - \langle \mathbf{D} \rangle \cdot \nabla\nabla\tilde{c} = -\tilde{\mathbf{v}}\nabla \cdot \langle c \rangle + \left\{ \nabla \cdot \left(\tilde{\mathbf{D}} \cdot \nabla \langle c \rangle\right) - \tilde{\mathbf{v}} \cdot \nabla \tilde{c} \right\} \tag{A38}$$

[49] The analysis of $\nabla \cdot (\tilde{\mathbf{D}} \cdot \nabla \langle c \rangle)$ is more difficult because of the mixture of length scales; however, if we consider the expanded form in comparison with $\tilde{\mathbf{v}} \cdot \nabla \langle c \rangle$

$$\tilde{\mathbf{v}} \cdot \nabla \langle c \rangle \gg \left(\nabla \cdot \tilde{\mathbf{D}}\right) \cdot (\nabla \langle c \rangle) + \tilde{\mathbf{D}} : \nabla\nabla \langle c \rangle \tag{A39}$$

we see that only the first term on the right hand side needs to be considered since

$$\left(\nabla \cdot \tilde{\mathbf{D}}\right) \cdot (\nabla \langle c \rangle) \gg \tilde{\mathbf{D}} : \nabla\nabla \langle c \rangle \tag{A40}$$

This indicates that we need only satisfy the restriction

$$\tilde{\mathbf{v}} \gg \nabla \cdot \tilde{\mathbf{D}} \tag{A41}$$

in order to simplify equation (A38) to the form

$$\frac{\partial \tilde{c}}{\partial t} + \langle \mathbf{v} \rangle \cdot \nabla \tilde{c} + \tilde{\mathbf{v}} \cdot \nabla \tilde{c} - \langle \mathbf{D} \rangle : \nabla\nabla \tilde{c} = -\tilde{\mathbf{v}} \cdot \nabla \langle c \rangle \tag{A42}$$

If we are to obtain an analytic solution for the closure problem, we are forced to impose the condition

$$\langle \mathbf{v} \rangle \cdot \nabla \tilde{c} \gg \tilde{\mathbf{v}} \cdot \nabla \tilde{c} \tag{A43}$$

and in general this will not be satisfied. However, again for the commonly adopted assumption that the variance of the log conductivity field is small (equation (A37)) the condition imposed by the inequality given by equation (A43) will generally be met.

A4. Timescales

[50] This restriction adopted in equation (39) is based on the idea that the timescale associated with changes in the volume averaged concentration, $\langle c \rangle$, is much larger than the timescale for the spatial deviation concentration, $\tilde{c}$. We can develop estimates for these characteristic times in terms of equation (17) for which we have included order of magnitude estimates leading to

$$\underbrace{\frac{\partial \langle c \rangle}{\partial t}}_{\mathrm{O}\left(\Delta\langle c \rangle / t^*_{\langle c \rangle}\right)} = \underbrace{\nabla \cdot (\langle \mathsf{D}(\mathbf{x}) \rangle \cdot \nabla \langle c \rangle)}_{\mathrm{O}\left(\mathrm{D}\Delta\langle c \rangle / L^2\right)} - \underbrace{\langle \mathbf{v}(\mathbf{x}) \rangle \cdot \nabla \langle c \rangle}_{\mathrm{O}\left(\langle \mathrm{v} \rangle \Delta \langle c \rangle / L\right)} - \nabla \cdot \langle \tilde{\mathbf{v}}(\mathbf{v}) \tilde{c} \rangle \tag{A44}$$

On the right hand side of this result we have estimates of the magnitudes for the smallest and largest terms, and these provide bounds on the characteristic time that are given by

$$\frac{L}{\langle \mathrm{v} \rangle} \leq t^*_{\langle c \rangle} \leq \frac{L^2}{\langle \mathrm{D} \rangle} \tag{A45}$$

For the spatial deviation concentration, we express the governing differential equation as

$$\underbrace{\frac{\partial \tilde{c}}{\partial t}}_{\mathrm{O}\left(\tilde{c}/t^*_{\tilde{c}}\right)} = \underbrace{\nabla \cdot (\mathbf{D}(\mathbf{x}) \cdot \nabla \tilde{c})}_{\mathrm{O}\left(\mathrm{D}\tilde{c}/\ell_{\mathrm{H}}^2\right)} - \underbrace{\mathbf{v}(\mathbf{x}) \cdot \nabla \tilde{c}}_{\mathrm{O}\left(\langle \mathrm{v} \rangle \tilde{c}/\ell_{\mathrm{H}}\right)} - \tilde{\mathbf{v}}(\mathbf{x}) \cdot \nabla \langle c \rangle + \left(\nabla \cdot \tilde{\mathbf{D}}(\mathbf{x})\right)(\nabla \langle c \rangle) \tag{A46}$$

These estimates provide bounds on the characteristic time that are given by

$$\frac{\ell_{\mathrm{H}}}{\langle \mathrm{v} \rangle} \leq t^*_{\tilde{c}} \leq \frac{\ell_{\mathrm{H}}^2}{\langle \mathrm{D} \rangle} \tag{A47}$$

When we compare equations (A45) and (A47), it is plausible to conclude that

$$t^*_{\langle c \rangle} \gg t^*_{\tilde{c}}, \quad \text{when L} \ll \ell_{\mathrm{H}} \tag{A48}$$

Appendix B: Solution of the Closure Problem for a Periodic Model

B1. Closure Problem

[51] The closure problem for a periodic unit cell is provided by equations (26a)–(26c) and is rewritten here for convenience.

$$\frac{\partial \tilde{c}}{\partial t} + \langle \mathbf{v} \rangle \cdot \nabla \tilde{c} - \langle \mathbf{D} \rangle : \nabla\nabla \tilde{c} = -\tilde{\mathbf{v}} \cdot \nabla \langle c \rangle \tag{B1a}$$

Initial condition

$$\tilde{c}(\mathbf{x}) = 0 \qquad \text{at } t = t_0 \tag{B1b}$$

Periodicity

$$\tilde{c}(\mathbf{x}) = 0\ \tilde{c}(\mathbf{x} - 1_i) \tag{B1c}$$

Averaging constraint

$$\langle \tilde{c} \rangle = 0 \tag{B2}$$

Typically, the closure problems that arise in the Eulerian problem formulation have been solved for infinite domains [e.g., *Gelhar*, 1993; *Cushman et al.*, 1995; *Deng and Cushman*, 1995a; *Fiori*, 1996], and this assumption implies that certain conditions must be met at infinity (although these boundary conditions are often not explicitly stated.) The method of volume averaging has conventionally been solved over a periodic domain. It is important to note that

neither of these two approximations truly represents reality, and that we should expect that for sufficiently large unit cells the two solutions should converge.

[52] Our goals for this appendix are (1) to determine an analytical solution to the closure problem for the periodic system defined above, and (2) to show that this solution is equivalent to the solution obtained for the infinite domain approximation as the period approaches infinity. In our developments, we will assume that the local dispersion tensor is constant and diagonal; this is assumption is consistent with available solutions for infinite systems [e.g., *Deng et al.*, 1993; *Fiori and Dagan*, 2000]. It will be convenient to write the conservation equation in the following form

Conservation equation for $\tilde{c}$

$$\frac{\partial \tilde{c}}{\partial t} + \langle \mathbf{v} \rangle \cdot \nabla \tilde{c} - \langle \mathbf{D} \rangle : \nabla \nabla \tilde{c} = G(\mathbf{x}, t) \tag{B3a}$$

$$G(\mathbf{x}, t) = -\tilde{\mathbf{v}} \cdot \nabla \langle c \rangle \tag{B3b}$$

For the remainder of this discussion, we will assume that the gradient of the average concentration can be taken as a constant over the unit cell. To generate a constraint indicating the conditions for which this approximation is true, expand $\nabla \langle c \rangle$ as a Taylor series

$$\nabla \langle c \rangle|_{\mathbf{x}+\mathbf{y}} = \nabla \langle c \rangle|_{\mathbf{x}} + \mathbf{y} \cdot \nabla \nabla \langle c \rangle|_{\mathbf{x}} + \ldots \tag{B4}$$

Clearly, we want to impose the condition that

$$\nabla \langle c \rangle|_{\mathbf{x}} \gg \mathbf{y} \cdot \nabla \nabla \langle c \rangle|_{\mathbf{x}} + \ldots \tag{B5}$$

Given the estimates

$$\mathbf{y} = \mathsf{O}(R_o), \qquad \nabla \nabla \langle c \rangle = \mathsf{O}(\nabla \langle c \rangle / L) \tag{B6}$$

we conclude that equation (B5) will be satisfied when

$$(R_o/L) \ll 1 \tag{B7}$$

This constraint on the closure problem is more severe than the length-scale constraint associated with the development of the volume averaged equation which is given by equation (9); however, the closure problem is only used to determine the effective dispersion tensor and errors in that parameter are not as serious as errors in the volume averaged solute transport equation.

[53] We will assume that the constraint given by equation (B7) is satisfied so that $\nabla \langle c \rangle$ can be taken as a (spatial) constant in the unit cell. Note that this approximation a priori assumes that the dispersive flux can be represented by a quasi-Fickian representation rather than a convolution-Fickian representation [*Deng and Cushman*, 1995a].

B2. Solution Via Finite Fourier Transforms

[54] We cannot use classical Fourier transform methods to obtain a solution to equations (B1a)–(B1c) because the concentration field does not approach zero as $\mathbf{x}$ approaches infinity (i.e., it is periodic). However, we can use finite Fourier transforms which follow directly from the theory of Fourier series. We will assume that the unit cell is a cube with sides of length (and, hence, period) $2p$. We define the finite Fourier transform by [*Churchill*, 1972, sect. 129]

$$\underline{f}(\mathbf{k}') = \mathcal{F}[f(\mathbf{x})] = \int_{V(p)} f(\mathbf{x}) \exp\left(-\frac{i\pi}{p}\mathbf{k}' \cdot \mathbf{x}\right) dV_x \tag{B8}$$

where $V(p)$ is $2p \times 2p \times 2p$ and dV_x is used to indicate that integration is carried out with respect to the components of $\mathbf{x}$. For notational convenience, we set

$$\mathbf{k} = \mathbf{k}'\pi/p \tag{B9}$$

so that the transform is defined

$$\underline{f}(\mathbf{k}) = \mathcal{F}[f(\mathbf{x})] = \int_{V(p)} f(\mathbf{x}) \exp(-i\mathbf{k} \cdot \mathbf{x}) dV_x \tag{B10}$$

Taking the transform of the deviation concentration, we find and expression that is similar to that generated by the conventional Fourier transform

$$\underline{\tilde{c}}(k_1, k_2, k_3, t) = \int_{-p}^{p} \int_{-p}^{p} \int_{-p}^{p} \tilde{c}(x, y, z, t) \cdot \exp(-ik_1 x) \exp(-ik_2 y) \cdot \exp(-ik_3 z) dx\, dy\, dz \tag{B11}$$

However, note that in equation (B1a) we will need the transforms of $\langle \mathbf{v} \rangle \cdot \nabla \tilde{c}$ and $\langle \mathbf{D} \rangle : \nabla \nabla \tilde{c}$. Because we have adopted a finite Fourier transform method, the transforms will be different from those for conventional Fourier transforms because of additional terms that arise from the boundaries. For example, consider

$$\mathcal{F}\left[\frac{\partial \tilde{c}}{\partial x}\right] = \int_{-p}^{p} \int_{-p}^{p} \int_{-p}^{p} \frac{\partial \tilde{c}}{\partial x} \exp(-ik_1 x) \cdot \exp(-ik_2 y) \exp(-ik_3 z) \cdot dx\, dy\, dz \tag{B12}$$

Using integration by parts, we can easily find the relation

$$\mathcal{F}\left[\frac{\partial \tilde{c}}{\partial x}\right] = ik_1 \underline{\tilde{c}} + \underline{M_x}(\mathbf{k}, t; p) \tag{B13}$$

where

$$\underline{M_x}(\mathbf{k}, t; p) = [\exp(-ik_1 p) - \exp(ik_1 p)] \int_{-p}^{p} \int_{-p}^{p} \tilde{c}(p, y, z, t) \cdot \exp(-ik_2 y) \exp(-ik_3 z) dy\, dz \tag{B14}$$

Here we have used the fact that $\tilde{c}(p, y, z) = \tilde{c}(-p, y, z)$. Note that we have the relationship

$$-[\exp(ik_1 p) - \exp(-ik_1 p)] = -2i \sin(k_1 p) = -2i \sin(k_1' \pi) \tag{B15}$$

Because k_1' takes only integer values, this term is identically zero. Thus, for periodic boundary conditions, the boundary terms vanish identically yielding a transform for the derivative that is the same as that obtained using conventional Fourier transforms

$$\mathcal{F}\left[\frac{\partial \tilde{c}}{\partial x}\right] = ik_1\underline{\tilde{c}} \tag{B16a}$$

Similarly, for the transforms of derivatives in the other variables we have

$$\mathcal{F}\left[\frac{\partial \tilde{c}}{\partial y}\right] = ik_2\underline{\tilde{c}} \tag{B16b}$$

$$\mathcal{F}\left[\frac{\partial \tilde{c}}{\partial z}\right] = ik_3\underline{\tilde{c}} \tag{B16c}$$

For the second-order derivatives that appear in the dispersion term, we can follow a similar approach to show that

$$\mathcal{F}\left[\frac{\partial^2 \tilde{c}}{\partial x^2}\right] = -k_1^2\underline{\tilde{c}} \tag{B17a}$$

$$\mathcal{F}\left[\frac{\partial^2 \tilde{c}}{\partial y^2}\right] = -k_2^2\underline{\tilde{c}} \tag{B17b}$$

$$\mathcal{F}\left[\frac{\partial^2 \tilde{c}}{\partial z^2}\right] = -k_3^2\underline{\tilde{c}} \tag{B17c}$$

[55] With these definitions, the finite Fourier transform of equation (3) can be found to be

$$\frac{d\underline{\tilde{c}}}{dt} + \langle \mathbf{v}\rangle \cdot i\mathbf{k}\underline{\tilde{c}} + \mathbf{k}\cdot\langle \mathbf{D}\rangle\cdot\mathbf{k}\underline{\tilde{c}} = \underline{G}(\mathbf{k}', t) \tag{B18}$$

where

$$\underline{G}(\mathbf{k}', t) = -\left\{\int_{V(p)} \exp\left(-\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{x}\right)\cdot\tilde{\mathbf{v}}(\mathbf{x})dV_x\right\}\cdot\nabla\langle c\rangle \tag{B19}$$

(recall that the constraint given by equation (B7) allows us to treat $\nabla\langle c\rangle$ as spatially constant in the unit cell). To make further progress, we take the Laplace transform of both sides of equation (B18), where the transform is defined by

$$g^\circ(s) = \mathrm{L}[g(t)] = \int_{t'=0}^{t'=\infty} f(t')\cdot\exp(-st')dt' \tag{B20}$$

to yield

$$[s + i\mathbf{k}\cdot\langle \mathbf{v}\rangle + \mathbf{k}\cdot\langle \mathbf{D}\rangle\cdot\mathbf{k}]\underline{\tilde{c}}^\circ = \underline{G}^\circ(\mathbf{k}, s) \tag{B21}$$

Note that except for the definition of the Fourier transform, this expression is mathematically identical (but with a different physical interpretation) to the expression derived by *Deng et al.* [1993, equation (8)]. Following their analysis we define

$$\underline{B}^\circ(\mathbf{k}, s) = [s + i\mathbf{k}\cdot\langle \mathbf{v}\rangle + \mathbf{k}\cdot\langle \mathbf{D}\rangle\cdot\mathbf{k}]^{-1} \tag{B22}$$

The transform-space solution can now be expressed

$$\underline{\tilde{c}}^\circ = \underline{B}^\circ(\mathbf{k}, s)\underline{G}^\circ(\mathbf{k}, s) \tag{B23}$$

[56] To put the solution given by equation (B23) in real time and space variables, we need only to invert the two types of integral transforms. The inverse of the Laplace transform is defined in the conventional way [*Churchill*, 1972], but the inverse of the finite Fourier transform is by a discrete sum rather than a continuous integral. The inverse transform of any function $\underline{f}(\mathbf{k})$ is given by

$$f(\mathbf{x}) = \frac{1}{(2p)^3}\sum_{k_3=-\infty}^{k_3=\infty}\sum_{k_2=-\infty}^{k_2=\infty}\sum_{k_1=-\infty}^{k_1=\infty}\underline{f}(k_1, k_2, k_3)\exp(ik_1x)\exp(ik_2y)\cdot\exp(ik_3z) \tag{B24}$$

Inverting equation (B23) and returning to the original variable $\mathbf{k}'$ defined by equation (B9) yields

$$\tilde{c}(\mathbf{x}, t) = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\exp\left(\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{x}\right)\cdot\int_{t'=0}^{t'=t}\underline{B}(\mathbf{k}', t-t')\underline{G}(\mathbf{k}', t')dt' \tag{B25}$$

Here we have used the convolution property of the Laplace transform

$$\mathcal{L}^{-1}(f^\circ(s)g^\circ(s)) = \int_0^t f(t-\tau)g(\tau)d\tau \tag{B26}$$

We can find the explicit Fourier-space expression for $\underline{B}$ by taking the inverse Laplace transform of equation (B22). This yields

$$\underline{B}(\mathbf{k}', t) = \exp\left(-\frac{i\pi}{p}\mathbf{k}'\cdot\langle \mathbf{v}\rangle t - \frac{\pi^2}{p^2}\mathbf{k}'\cdot\langle \mathbf{D}\rangle\cdot\mathbf{k}'t\right) \tag{B27}$$

Substituting this expression into equation (B25) yields

$$\tilde{c}(\mathbf{x}, t) = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\exp\left(\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{x}\right)\cdot\int_0^t\exp\left(-(t-t')\frac{i\pi}{p}\mathbf{k}'\cdot\langle \mathbf{v}\rangle - (t-t')\frac{\pi^2}{p^2}\mathbf{k}'\cdot\langle \mathbf{D}\rangle\cdot\mathbf{k}'\right)\cdot\left[\int_{V(p)}\exp\left(-\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{z}\right)\tilde{\mathbf{v}}(\mathbf{z})dV_z\right]dt'\cdot\nabla\langle c\rangle \tag{B28}$$

To be consistent with the development of the quasi-Fickian flux presented by *Deng and Cushman* [1995a], we have

assumed that $\nabla\langle c\rangle$ can be treated as constant for the purposes of conducting integration in time; we will delay the development of an appropriate constraint for now. Conducting the integration in time and combining the two exponential functions yields a series solution for the periodic boundary value problem of the form

Solution for the deviation concentration

$$\tilde{c}(\mathbf{x},t) = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')} \cdot \int_{V(p)} \exp\left[-\frac{i\pi}{p}\mathbf{k}'\cdot(\mathbf{z}-\mathbf{x})\right]\tilde{\mathbf{v}}(\mathbf{z})dV_z\cdot\nabla\langle c\rangle \tag{B29a}$$

where

$$\beta(\mathbf{k}') = \frac{i\pi}{p}\mathbf{k}'\cdot\langle\mathbf{v}\rangle + \frac{\pi^2}{p^2}\mathbf{k}'\cdot\langle\mathbf{D}\rangle\cdot\mathbf{k}' \tag{B29b}$$

Note that equation (B29a) can be put in the form

General solution form for the closure problem

$$\tilde{c}(\mathbf{x},t) = \mathbf{b}(\mathbf{x},t)\cdot\nabla\langle c\rangle \tag{B30}$$

This form is commonly adopted for the representation of the general solution to the closure problem in the method of volume averaging [e.g., *Whitaker*, 1999, chap. 1]. For this representation, we have made the correspondence

$$\mathbf{b}(\mathbf{x},t) = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')} \cdot \int_{V(p)} \exp\left[-\frac{i\pi}{p}\mathbf{k}'\cdot(\mathbf{z}-\mathbf{x})\right]\tilde{\mathbf{v}}(\mathbf{z})dV_z \tag{B31}$$

B3. Development of the Effective Dispersion Tensor: Comparison With Previous Solutions

[57] Equation (B29) represents the series solution for the perturbation concentration, subject to the approximations specified above. Although this represents a solution for the deviation concentration, we ultimately need the averaged quantity $\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle$. Toward this end, we multiply both sides of equation (B29a) on the left by $\tilde{\mathbf{v}}(\mathbf{x})$ and average, yielding

$$\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')} \times \int_{V(p)} \exp\left[-\frac{i\pi}{p}\mathbf{k}'\cdot(\mathbf{z}-\mathbf{x})\right]\langle\tilde{\mathbf{v}}(\mathbf{z})\tilde{\mathbf{v}}(\mathbf{x})\rangle dV_z\cdot\nabla\langle c\rangle \tag{B32}$$

When the velocity field can be assumed to be second-order stationary and ergodic (in the sense of *Cushman* [1983]), the volume average covariance $\langle\tilde{\mathbf{v}}(\mathbf{z})\tilde{\mathbf{v}}(\mathbf{x})\rangle$ can be approximated as being a tensor that depends only upon the relative separation $\mathbf{y} = \mathbf{z} - \mathbf{x}$. Making this substitution, we find

$$\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')} \cdot \left\{\int_{V_{(p)}} \exp\left[-\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{y}\right]\cdot\mathbf{R}(\mathbf{y})dV_y\right\}\cdot\nabla\langle c\rangle \tag{B33}$$

where dV_y is used to indicate that integration is carried out with respect to the components of $\mathbf{y}$. Realizing that the last integral on the right-hand side of equation (B33) is just the Fourier transform of the covariance tensor, we have

Solution for the effective dispersion tensor in periodic systems

$$\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle = \frac{1}{(2p)^3}\sum_{k_3'=-\infty}^{k_3'=\infty}\sum_{k_2'=-\infty}^{k_2'=\infty}\sum_{k_1'=-\infty}^{k_1'=\infty}\frac{1-\exp[-\beta(\mathbf{k}')t]}{\beta(\mathbf{k}')} \cdot \underline{\mathbf{R}}(\mathbf{k}')\cdot\nabla\langle c\rangle \tag{B34}$$

where

$$\underline{\mathbf{R}}(\mathbf{k}') = \int_{V(p)} \exp\left[-\frac{i\pi}{p}\mathbf{k}'\cdot\mathbf{y}\right]\mathbf{R}(\mathbf{y})dV_y \tag{B35}$$

$$R(\mathbf{y}) = \langle\tilde{\mathbf{v}}(\mathbf{y}+\mathbf{x})\tilde{\mathbf{v}}(\mathbf{x})\rangle \tag{B36}$$

[58] Note that although the solution given by equation (B34) is in terms of a discrete sum rather than a continuous integral, the solution is reminiscent of that provided by *Deng and Cushman* [1995a, equation (13)] which was developed for an infinite domain. An exact equivalence can be found by letting the period p tend toward infinity. To accomplish this, we first return to the substitution $\mathbf{k} = \mathbf{k}'\pi/p$ first given in equation (B9). We write this as

$$\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle = \frac{1}{(2\pi)^3}\sum_{k_3=-\infty}^{k_3=\infty}\sum_{k_2=-\infty}^{k_2=\infty}\sum_{k_1=-\infty}^{k_1=\infty}\frac{1-\exp[-\beta(\mathbf{k})t]}{\beta(\mathbf{k})} \cdot \left\{\int_{V(p)} \exp(-i\mathbf{k}\cdot\mathbf{y})\{\tilde{\mathbf{v}}(\mathbf{y}+\mathbf{x})\tilde{\mathbf{v}}(\mathbf{x})\}dV_y\right\} \cdot\nabla\langle c\rangle(\pi/p)^3 \tag{B37}$$

Note that as $p\to\infty$ this sum tends toward an integral [e.g., *Wiener*, 1933] of the form

$$\langle\tilde{c}(\mathbf{x},t)\tilde{\mathbf{v}}(\mathbf{x})\rangle = \left\{\frac{1}{(2\pi)^3}\int_{R^3}\frac{1-\exp[-\beta(\mathbf{k})t]}{\beta(\mathbf{k})}\underline{\mathbf{R}}'(\mathbf{k})dV_k\right\}\cdot\nabla\langle c\rangle \tag{B38}$$

Here dV_k is used to indicate that integration is carried out with respect to the components $\mathbf{k}$ and $\underline{\mathbf{R}}'(\mathbf{k})$ is the Fourier transform of the spatially stationary covariance function in an unbounded domain. For velocity fields that are ergodic in the sense of *Cushman* [1983], the volume average and the ensemble average can be considered equivalent as the averaging volume becomes infinite; under these conditions equation (6) is identical to the quasi-Fickian result of *Deng and Cushman* [1995a, equation (13)]. It is worth noting that this result is also equivalent to the effective dispersion tensor developed from the Lagrangian perspective that has been recently presented by *Fiori and Dagan* [2000]. This result can be recovered by taking the time derivative of equation (14) of that work.

Appendix C: Solution for the Variance of D_{11}

[59] An analytical expression for the asymptotic value of the variance of the effective diffusion tensor as a function of

the scale of observation has been developed previously by *Fiori* [1998] using ensemble averaging techniques. For the case $Pe \rightarrow \infty$, the solution for the two-dimensional case is given by *Fiori* [1998], and can be put in the form (A. Fiori, personal communication):

$$\lambda = \| b_2/I_Y \| \tag{C1}$$

$$d_{11}(\lambda) = \lambda K_1(\lambda)\sigma_Y^2 U I_Y \tag{C2}$$

$$r_{11}(\lambda) = \pi[K_1(\lambda)L_0(\lambda) + L_1(\lambda)K_0(\lambda)] + 2K_2(\lambda) - 4/\lambda^2 \tag{C3}$$

$$\begin{aligned}\sigma^2_{D11,\infty} = {} & 2r^2_{11}(\lambda) + 4/\lambda^2 \int_0^\lambda (\lambda - a')d^2_{11}(a')da' \\ & - 8/\lambda^3 \int_0^\lambda \int_0^{\lambda - a'} (\lambda - a' - a'')d_{11}(a')d_{11}(a'')da''da' \\ & - 16/\lambda^3 \int_0^\lambda \int_0^{a'} (\lambda - a')d_{11}(a')d_{11}(a'')da''da'\end{aligned} \tag{C4}$$

Note that this is a correction (and additional elucidation) from the original work by *Fiori* [1998, equations (9) and (14)]. Here b_2 is the spatial coordinate in the direction transverse to the mean flow direction (and should be thought of as the initial transverse size of the solute plume or equivalently the observation scale of the dispersion process), λ is the spatial coordinate normalized by the integral scale, d_{11} is the longitudinal component of the asymptotic effective dispersion tensor, r_{11} is the rate of growth of the plume centroid location variance in the longitudinal direction (assuming and exponential log conductivity covariance for the lognormal conductivity field [cf. *Dagan*, 1991]), and $\sigma^2_{D11,\infty}$ is the asymptotic value of the variance of the longitudinal component (D_{11}) of the effective dispersion tensor. The functions K_0, K_1, and K_2 are modified Bessel functions, and L_0 and L_1 are modified Struve functions.

Notation

$\mathbf{b}(\mathbf{x}, t)$ vector defined by equation (37) that maps the perturbation concentration field onto the average concentration field for closure, m.

c intrinsic Darcy-scale concentration (defined per unit fluid volume), mol m^{-3}.

$\langle c \rangle$ volume average concentration, mol m^{-3}.

$\tilde{c}$ $= c - \langle c \rangle$, concentration deviation, mol m^{-3}.

$\underline{\tilde{c}}$ finite Fourier transform of the concentration deviation.

$\underline{\tilde{c}}^\circ$ both finite Fourier and Laplace transform of the concentration deviation.

C_{xx} volume averaged covariance function, defined by equation (42).

$CV_{D,11}$ coefficient of variation for $\mathsf{D}_{eff},_{11}$, defined by equation (49a).

$CV_{D,22}$ coefficient of variation for $\mathsf{D}_{eff},_{22}$, defined by equation (49b).

$\mathbf{D}(\mathbf{x})$ Darcy-scale dispersion tensor, m^2 s^{-1}.

$\mathsf{D}_{eff},_{11}$ (1, 1) component of the Darcy-scale dispersion tensor, m^2 s^{-1}.

$\mathsf{D}_{eff},_{22}$ (2, 2) component of the Darcy-scale dispersion tensor, m^2 s^{-1}.

$\langle \mathbf{D} \rangle$ Volume average Darcy-scale dispersion tensor, m^2 s^{-1}.

$\tilde{\mathbf{D}}(\mathbf{x})$ $= \mathbf{D}(\mathbf{x}) - \langle \mathbf{D} \rangle$ Dispersion deviation tensor, m^2 s^{-1}.

$\mathbf{D}_{eff}(t)$ Volume average effective dispersion tensor defined analytically by equation (33), or in numerical applications by equation (46), m^2 s^{-1}.

$\mathbf{D}^\infty_{eff}(t)$ Effective (macroscopic) dispersion tensor for an infinite domain (under ergodic conditions, arising from either an ensemble or volume average), defined by equation (34), m^2 s^{-1}.

$\overline{\mathbf{D}}_{eff}(t)$ Volume average effective dispersion tensor averaged over an ensemble of realizations of unit cells, m^2 s^{-1}.

$\mathsf{D}_{eff},_{11}$ (1, 1) component of $\overline{\mathbf{D}}_{eff}$ defined by equation (47a), m^2 s^{-1}.

$\mathsf{D}_{eff},_{22}$ (2, 2) component of $\overline{\mathbf{D}}_{eff}$ defined by equation (47b), m^2 s^{-1}.

I_Y integral scale defined by equation (41), m^2.

$K(\mathbf{x})$ hydraulic conductivity field, m^2 s^{-1}.

$K_G(\mathbf{x})$ $= \ln(Y_0)$, geometric mean hydraulic conductivity field, m^2 s^{-1}.

$\mathbf{k}'$ Fourier space variable.

$\mathbf{k}$ $\mathbf{k} = \mathbf{k}'\pi/p$, transformed Fourier space variable.

ℓ_H characteristic length scale associated with Darcy-scale conductivity perturbations, m.

L characteristic length scale associated with volume averaged quantities, m.

n Darcy-scale fluid volume fraction (porosity).

N number of realizations in an ensemble of unit cells.

p period of a spatially periodic unit cell, m.

R_o radius of the macroscopic averaging volume, V, illustrated in Figure 1 (level II), m.

$\mathbf{R}(\mathbf{y})$ $= \langle \tilde{\mathbf{v}}(\mathbf{y} + \mathbf{x})\tilde{\mathbf{v}}(\mathbf{x}) \rangle$ (spatially stationary) velocity covariance function, m^2 s^{-2}.

$\underline{\mathbf{R}}(\mathbf{k}')$ finite Fourier transform of the velocity covariance function defined by equation (30).

$\mathbf{v}(\mathbf{x})$ intrinsic Darcy-scale velocity (seepage velocity), m^2 s^{-1}.

$\langle \mathbf{v} \rangle$ volume average intrinsic velocity, m^2 s^{-1}.

$\tilde{\mathbf{v}}(\mathbf{x})$ $= \mathbf{v}(\mathbf{x}) - \langle \mathbf{v}(\mathbf{x}) \rangle$, volume average velocity perturbation, m^2 s^{-1}.

$V(p)$ volume of a cubic unit cell of period p, m^3.

V macroscopic averaging volume (Figure 1, Level II), m^3.

$Y(\mathbf{x})$ $= \ln[K(\mathbf{x})]$, the log transform of the hydraulic conductivity.

$Y_0(\mathbf{x})$ ensemble mean of the log transform hydraulic conductivity.

$Y'(\mathbf{x})$ $= Y - Y_0$, deviation of the log transform of the hydraulic conductivity.

$\langle Y'(\mathbf{x})Y'(\mathbf{x}')\rangle_E$ ensemble averaged covariance function, defined by equation (40).

$\langle Y'(\mathbf{x})Y'(\mathbf{x}')\rangle$ volume averaged covariance function, defined by equation (42).

α_L longitudinal dispersivity, m.

α_T transverse dispersivity, m.

$\beta(\mathbf{k}')$ Fourier transform of the mean transport operator defined in equation (31).

$\sigma^2_{D,11}$ variance of $\mathsf{D}_{eff},_{11}$ defined by equation (48a).

$\sigma^2_{D,11}$ variance of $\mathsf{D}_{eff},_{11}$ defined by equation (48b).

$\boldsymbol{\sigma}^2_D$ variance tensor for $\mathbf{D}_{eff}$ defined (analytically) by equation (51).

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