

Analysis of macrodispersion through volume-averaging: Moment equations

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Abstract: Macrodispersion is spreading of a substance induced by spatial variations in local advective velocity at field scales. Consider the case that the steady-state seepage velocity and the local dispersion coefficients in a heterogeneous formation may be modeled as periodic in all directions in an unbounded domain. The equations satisfied by the first two spatial moments of the concentration are derived for the case of a conservative non-reacting solute. It is shown that the moments can be calculated from the solution of well-defined deterministic boundary value problems. Then, it is described how the rate of increase of the first two moments can be calculated at large times using a Taylor-Aris analysis as generalized by Brenner. It is demonstrated that the second-order tensor of macrodispersion (or effective dispersion) can be computed through the solution of steady-state boundary-value problems followed by the determination of volume averages. The analysis is based solely on volume averaging and is not limited by the assumption that the fluctuations are small. The large-time results are valid when the system is in a form of equilibrium in which a tagged particle samples all locations in an appropriately defined "phase space" with equal probability.

Key words: Solute transport, Heterogeneity, Dispersion.

1 Introduction

Macrodispersion, or spreading due to variability in local advective velocity, has attracted much attention recently in the geohydrologic literature. It has been studied in the works of Gelhar et al. (1979), Gelhar and Axness (1983), Gelhar (1986), Dagan (1982, 1984, 1987), Schwarz (1977), Smith and Schwarz (1980), Matheron and DeMarsily (1980), Dieulin et al. (1981), Sposito et al. (1986), Neuman et al. (1987), and Kitanidis (1988), to mention some of the most relevant articles. (Additional references can be found in the recent book of Dagan (1989), Cushman (1990), and the review paper of Wheatcraft and Cushman (1991).) These works have shed light on the mechanism of macrodispersion, have explained the large rates of spreading observed in heterogeneous formations at field scales, and have suggested methods for the calculation of rates of spreading from statistics of spatial variability of velocity or conductivity.

Most of the work on macrodispersion has dealt with "random media", i.e., disordered media with statistically specified parameters. However, the quantitative analysis of macroscopic transport properties in such media is fraught with difficulties. The most commonly used methods are Monte Carlo simulations and small-perturbation (or first-order) approximations. The former can be extremely expensive and yields results which cannot be readily generalized to cases with attributes different from those of the specific experiment. The latter is applicable to cases with small variance. No computationally efficient method is available to calculate macrodispersivities for all variances.

This paper is perhaps most closely related to the works of Gelhar et al. (1979), Gelhar and Axness (1983), and Neuman et al. (1987). These works have computed the large-time macroscopic dispersion coefficients for stationary variability of advective velocity using ensemble averaging and assuming small fluctuations. Cushman (1983) disputed on theoretical grounds the validity of the small-perturbation approach. Numerical experiments for a simple case have indicated that the underlying assumption in the small-perturbation assumption may lead to incorrect results when the variance of the velocity is not actually small (Kitanidis, 1988). According to Dagan (1989, p. 335) the applicability of the small-perturbation approach is limited to small values of the variance of log-conductivity and the "development of an adequate nonlinear theory or efficient numerical procedures is a challenging topic for future research."

The present work is an attempt to develop such a theory. A major objective was to reduce the problem into a form which allows the application of efficient numerical methods for the computation of macroscopic transport coefficients. Following an analytical approach, it is shown that the computation can be reduced to the solution of an elliptic boundary value problem and an integration. Another objective was to develop a better physical insight into what these macrodispersion coefficients really mean by adopting a volume-averaging approach instead of the usual ensemble averaging approach. I believe that the volume-averaging approach offers insights which are impossible with other available methods.

In modeling macrodispersion, the important feature is spatial variability of the local advective velocity at the Darcy scale. Most works adopt two basic assumptions. The first assumption is that this velocity varies from point to point but, in a sense, repeats itself in space ("translational invariance"). The second assumption is that the length scale of velocity fluctuations is much smaller than the field scale ("disparity of scales"). When velocity variability is represented through the formalism of stationary random fields, this repetition is of a statistical nature. Thus, volume averages of stationary parameters are not constant and independent of the location unless the volume tends to infinity. The stationary model is quite general and has rightfully been adopted in the above mentioned works. However, this generality comes at a cost. The main difficulty, as I see it, is that there is no finite volume that could serve as a "phase space", in the sense of classical statistical mechanics (see Reif (1967)). As a consequence: (a) The derivation of the equations satisfied by the macroscopic transport coefficients is rather cumbersome; (b) numerical methods are not well suited for problems defined over infinite domains. A way to deal with both difficulties is to temporarily replace the stationary functions with periodic functions. Once the result has been obtained through volume-averaging over a finite volume, it can be extended from the periodic to the stationary model by taking the limit of the volume to infinity. In terms of the application of numerical methods, the results may be approximated to any desirable degree of accuracy by sufficiently increasing the period. This approach has been adopted for different but related problems (Van Lent and Kitanidis, 1989; Kitanidis, 1990).

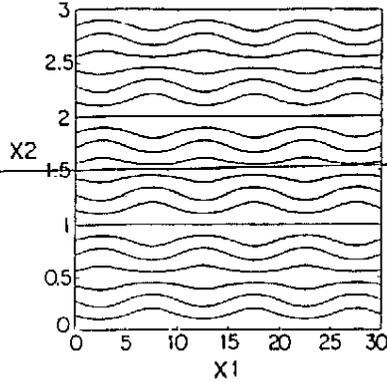


Figure 1

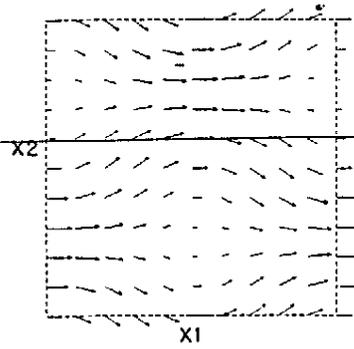


Figure 2

Figure 1. Streamlines in a hypothetical periodic medium. The period in the x_1 direction is 10 and in the x_2 direction is 1

Figure 2. Velocity vectors showing the movement of particles within the phase space

In this paper, the equations satisfied by the macrodispersion coefficients are derived for a formation with periodic parameters. Volume-averaging methods on periodic media have found many applications in heterogeneous porous media. Examples (containing many references) are the works of Whitaker (1967), Plumb and Whitaker (1988), and Bear and Bachmat (1990). The model adopted in the present work is similar to the one previously adopted by Bhattacharya (1985) and Gupta and Bhattacharya (1986) but the derivation and the physical meaning are different and the result is more general since it accounts for variability in local dispersion coefficients. In another paper, the results are extended to the cases of stationary random media.

2 The problem

2.1 Velocity and local dispersion coefficients

Consider steady flow with seepage velocity which is a periodic function in all three directions. Let l_i be the period in direction i . That is,

$$\mathbf{u}(X_1, X_2, X_3) = \mathbf{u}(X_1 + m_1 l_1, X_2 + m_2 l_2, X_3 + m_3 l_3) \quad (1)$$

where $\mathbf{u} = (u_1, u_2, u_3)$ is the vector of seepage velocity (specific discharge over effective porosity); $\mathbf{X} = (X_1, X_2, X_3)$ are the spatial coordinates in a global Cartesian coordinate system, and $m_1, m_2,$ and m_3 are integers. Figure 1. depicts the streamlines in a periodic medium. The analysis is carried out for a three-dimensional flow domain but also applies to two-dimensional flow. Furthermore, the velocity function is continuous and satisfies the condition:

$$\frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} + \frac{\partial u_3}{\partial x_3} = 0 \quad (2)$$

This last assumption is commonly made in dispersion studies (e.g., Gelhar and Axness, 1983). For example, this condition is satisfied from continuity of an incompressible fluid in a porous formation of constant porosity. In this paper, this condition is important only in determining the large-time behavior.

Consider now that we superimpose a rectangular grid with spacing l_i in direction i . The grid subdivides the domain into elements, each shaped like a rectangular

parallelepiped with lengths of sides l_1, l_2 , and l_3 . Assuming that the origin of the global coordinate system coincides with the center of symmetry of an element, the coordinates of the center of any element are $(n_1 l_1, n_2 l_2, n_3 l_3)$ where $n_1, n_2, n_3 = \dots, -2, -1, 0, 1, 2, \dots$. Consequently, each element is identified with a triplet of integers (n_1, n_2, n_3) , or \bar{n} .

For the sake of convenience, a system of local coordinates (x_1, x_2, x_3) will be introduced for each element. The origin of this Cartesian system is at the center of the element and the three axes are parallel to the axes of the global system. Now each point with global coordinates $\mathbf{X} = (X_1, X_2, X_3)$ can be represented as $(\bar{n}, \mathbf{x}) = (n_1, n_2, n_3, x_1, x_2, x_3)$ where $\bar{n} = (n_1, n_2, n_3)$ specifies the element and $\mathbf{x} = (x_1, x_2, x_3)$ specifies the location within the element. The relation between global and local coordinates is given by

$$X_i = n_i l_i + x_i, \quad i = 1, 2, 3 \quad (3)$$

where, in this work, n_1, n_2, n_3 are always integers and x_1, x_2 , and x_3 always satisfy the conditions $-l_1/2 \leq x_1 \leq l_1/2$, $-l_2/2 \leq x_2 \leq l_2/2$ and $-l_3/2 \leq x_3 \leq l_3/2$.

Consider now a point on the interface of elements (n_1, n_2, n_3) and $(n_1 + 1, n_2, n_3)$. From continuity of the velocity,

$$u(n_1, n_2, n_3, l_1/2, x_2, x_3) = u(n_1 + 1, n_2, n_3, -l_1/2, x_2, x_3) \quad (4)$$

Similarly, on the interface of elements (n_1, n_2, n_3) and $(n_1, n_2 + 1, n_3)$,

$$u(n_1, n_2, n_3, x_1, l_2/2, x_3) = u(n_1, n_2 + 1, n_3, x_1, -l_2/2, x_3) \quad (5)$$

and, at the interface of elements (n_1, n_2, n_3) and $(n_1, n_2, n_3 + 1)$,

$$u(n_1, n_2, n_3, x_1, x_2, l_3/2) = u(n_1, n_2, n_3 + 1, x_1, x_2, -l_3/2) \quad (6)$$

The velocity at local coordinates \mathbf{x} is the same for all elements, because of the periodicity of the velocity function. Thus, we may suppress the dependence of velocity on the number of the element and show only the dependence on the local coordinates

$$u(n_1, n_2, n_3, x_1, x_2, x_3) = u(x_1, x_2, x_3) \quad (7)$$

where the following conditions are due to continuity

$$\begin{aligned} u(l_1/2, x_2, x_3) &= u(-l_1/2, x_2, x_3); & u(x_1, l_2/2, x_3) &= u(x_1, -l_2/2, x_3); \\ u(x_1, x_2, l_3/2) &= u(x_1, x_2, -l_3/2) \end{aligned} \quad (8)$$

We will refer to such conditions as the requirements of symmetry.

Because of equations (8) and mass conservation, it is straightforward to verify that

$$\begin{aligned} \frac{1}{l_2 l_3} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} u_1(-l_1/2, x_2, x_3) dx_2 dx_3 &= \frac{1}{l_2 l_3} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} u_1(x_1, x_2, x_3) dx_2 dx_3 \\ &= \frac{1}{l_1 l_2 l_3} \int_V u_1(x_1, x_2, x_3) dx = \bar{u}_1 \end{aligned} \quad (9)$$

where V is the volume of an element, dx stands for $dx_1 dx_2 dx_3$, and \bar{u}_1 is the average velocity in the x_1 direction. This result allows the substitution of areal averages of velocity by volume averages. Similar relations hold for u_2 and u_3 .

The microdispersion (or local-dispersion) coefficients is also assumed periodic, with the same periods as the seepage velocity.

2.2 Concentration

Let $c(X_1, X_2, X_3, t)$ or, in local coordinates, $c(n_1, n_2, n_3, x_1, x_2, x_3, t)$ be the concentration of a conservative-nonreactive solute. For the sake of convenience and without loss of generality, consider that the solute has unit "mass" over the infinite domain V_∞ , i.e.,

$$\int_{V_\infty} c(X, t) dX = 1 \quad (10)$$

In this case, the concentration function can also be interpreted as the probability density function of the location occupied by a tagged particle at time t .

The solute is advected by the moving fluid and at the same time undergoes microdispersion. This microdispersion (or laboratory-scale dispersion) can be described qualitatively as spreading due to wandering of the solute particles in tortuous flow paths as well as velocity variations from the shear effect induced by the soil matrix (see Fried, 1975, p. 7, Freeze and Cherry, 1979, p. 75). That is, microdispersion is induced by pore-scale variations of fluid velocity as well as Brownian motion. It is assumed that at the Darcy scale, which is much larger than that of the pores but small than the scale of the heterogeneities of the medium, microdispersion (including the usually less important molecular diffusion) is a Fickian process with dispersion second-order tensor D .

Within each element, the conservation equation can be written in the familiar form, known as the advection-dispersion equation,

$$\frac{\partial c}{\partial t} + \nabla \cdot (uc) - \nabla \cdot (\nabla c) = 0 \quad (11)$$

where ∇ is the vector differential operator $\nabla = (\partial/\partial x_1, \partial/\partial x_2, \partial/\partial x_3)^T$, with respect to the local coordinates. $\nabla \cdot$ denotes the divergence of the 3-dimensional vector which follows. For example, $\nabla \cdot u = \partial u_1/\partial x_1 + \partial u_2/\partial x_2 + \partial u_3/\partial x_3$. ∇ not followed by a dot indicates the gradient of the scalar quantity which follows. For example, ∇c , where c is a scalar, is the 3-dimensional vector $(\partial c/\partial x_1, \partial c/\partial x_2, \partial c/\partial x_3)^T$. Equation (11) has assumed that u and D are not affected by c (i.e., the flow and the microdispersion are not affected by the concentration). Also that no mass is added or subtracted after the initial time.

Equation (11) is satisfied in the interior of each element. At the interface of two adjacent elements, it is required that the flux across the interface should be the same no matter what system of local coordinates it is calculated in. Consider the interface between elements (n_1, n_2, n_3) and $(n_1 + 1, n_2, n_3)$. The advective flux across the interface at any point is

$$\begin{aligned} & u_1(l_1/2, x_2, x_3)c(n_1, n_2, n_3, l_1/2, x_2, x_3, t) \\ & = u_1(-l_1/2, x_2, x_3)c(n_1 + 1, n_2, n_3, -l_1/2, x_2, x_3, t) \end{aligned} \quad (12a)$$

which, given (8), means that the concentration must be continuous at the interface

$$c(n_1, n_2, n_3, l_1/2, x_2, x_3, t) = c(n_1 + 1, n_2, n_3, -l_1/2, x_2, x_3, t) \quad (12b)$$

Similarly, at the other two interfaces:

$$c(n_1, n_2, n_3, x_1, l_2/2, x_3, t) = c(n_1, n_2 + 1, n_3, x_1, -l_2/2, x_3, t) \quad (13)$$

$$c(n_1, n_2, n_3, x_1, x_2, l_3/2, t) = c(n_1, n_2, n_3 + 1, x_1, x_2, -l_3/2, t) \quad (14)$$

It is also required that the dispersive flux is the same. Thus, the gradient of the concentration on each interface must be continuous:

$$\frac{\partial c}{\partial x_i} \Big|_{n_1, n_2, n_3, l_1/2, x_2, x_3, t} = \frac{\partial c}{\partial x_i} \Big|_{n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t} \quad (15)$$

$$\frac{\partial c}{\partial x_i} \Big|_{n_1, n_2, n_3, x_1, l_2/2, x_3, t} = \frac{\partial c}{\partial x_i} \Big|_{n_1, n_2+1, n_3, x_1, -l_2/2, x_3, t} \quad (16)$$

$$\frac{\partial c}{\partial x_i} \Big|_{n_1, n_2, n_3, x_1, x_2, l_3/2, t} = \frac{\partial c}{\partial x_i} \Big|_{n_1, n_2, n_3+1, x_1, x_2, -l_3/2, t} \quad (17)$$

where i takes the values 1, 2, or 3. Finally, the concentration at very large distances from the origin vanishes:

$$c(n_1, n_2, n_3, x_1, x_2, x_3, t) = 0 \quad \text{as } n_1, n_2, n_3 \rightarrow \pm\infty \quad (18)$$

It will be assumed that the rate of decrease is such that all spatial moments can be defined.

3 Spatial moments

Determining the concentration is difficult when the seepage velocity is spatially variable. A general method first proposed by Aris (1956) and used in numerous studies (e.g., Barton, 1983; Güven et al., 1984, Brenner, 1980a, 1980b, 1982a, 1982b) is to deal with spatial moments of c . Actually, we will deal with two types of moments, local and global.

Local moments depend on the vector of local coordinates as well as on time. The zero-order moment is a scalar defined as the sum of concentrations at all points with local coordinates \mathbf{x} ,

$$a(\mathbf{x}, t) = \sum_{\mathbf{n}} c(\mathbf{n}, \mathbf{x}, t) \quad (19)$$

where $\sum_{\mathbf{n}}$ is shorthand notation for the triple summation $\sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty}$. According to the interpretation of c as a pdf, $a(\mathbf{x}, t)$ is the probability that at time t a tagged particle occupies a location with local coordinates \mathbf{x} .

The first moment is a three-dimensional vector $\mathbf{b}(\mathbf{x}, t)$ whose i^{th} element is defined as follows:

$$b_i = (\mathbf{b}(\mathbf{x}, t))_i = \sum_{\mathbf{n}} (n_i l_i) c(\mathbf{n}, \mathbf{x}, t) \quad (20)$$

For example,

$$b_1 = l_1 \sum_{\mathbf{n}} n_1 c(n_1, n_2, n_3, x_1, x_2, x_3, t) \quad (21)$$

The second moment is a 3x3 symmetrical tensor whose ij^{th} element is defined as follows

$$C_{ij} = (C(\mathbf{x}, t))_{ij} = \sum_{\mathbf{n}} (n_i l_i)(n_j l_j) c(\mathbf{n}, \mathbf{x}, t) \quad (22)$$

For example,

$$C_{11} = l_1^2 \sum_{\mathbf{n}} n_1^2 c(n_1, n_2, n_3, x_1, x_2, x_3, t) \quad (23)$$

and

$$C_{12} = l_1 l_2 \sum_{\mathbf{n}} n_1 n_2 c(n_1, n_2, n_3, x_1, x_2, x_3, t) \quad (24)$$

and so on. Higher moments could be defined in a similar way but they will not be required in this analysis.

Global moments are defined from the intergral of local moments over the local coordinates. That is,

$$\alpha(t) = \int_V a(\mathbf{x}, t) d\mathbf{x} ; \beta(t) = \int_V \mathbf{b}(\mathbf{x}, t) d\mathbf{x} ; \text{ and } \Gamma(t) = \int_V C(\mathbf{x}, t) d\mathbf{x} \quad (25-27)$$

Consider the physical meaning of the global moments. For each element \mathbf{n} , define \bar{c} as

$$\bar{c}(\mathbf{n}, t) = \int_V c(\mathbf{n}, \mathbf{x}, t) d\mathbf{x} \quad (28)$$

This is the "mass" of solute in element \mathbf{n} at time t and can be interpreted as the probability that a tagged particle is in element \mathbf{n} at time t . If this mass or probability is assumed concentrated at the center of the element, then α , β , Γ are the spatial moments. The zero moment, α , represents the total mass and is equal to 1 at all times (see Equation 10). The first moment, $\beta(t)$, is the vector of coordinates of the centroid (center of mass) of the plume and can be written

$$\beta(t) = \sum_{\mathbf{n}} \bar{c}(\mathbf{n}, t) \mathbf{X}(\mathbf{n}) \quad (29)$$

where $\mathbf{X}(\mathbf{n})$ is the vector of global coordinates of the center of element \mathbf{n} .

The second moment is the tensor of the mean square displacements about the origin of the global coordinate system and can be written

$$\Gamma(t) = \sum_{\mathbf{n}} \bar{c}(\mathbf{n}, t) \mathbf{X}(\mathbf{n}) \mathbf{X}(\mathbf{n})^T \quad (30)$$

To measure the spreading of the plume about the center of mass of the plume, define the central second global moment

$$\Delta(t) = \sum_{\mathbf{n}} \bar{c}(\mathbf{n}, t) (\mathbf{X}(\mathbf{n}) - \beta(t)) (\mathbf{X}(\mathbf{n}) - \beta(t))^T = \Gamma(t) - \beta(t) \beta(t)^T \quad (31)$$

It is important to keep in mind that the global moments are defined for concentration after averaging within each element. The implications of this averaging will be discussed later.

4 Equations satisfied by the local moments

First off, we obtain the equations satisfied by the local moments. For fixed \mathbf{x} , summation over all elements gives:

$$\sum_{\mathbf{n}} \left\{ \frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{u}c) - \nabla \cdot (\mathbf{D}\nabla c) \right\} = \tilde{0} \quad (32)$$

Since neither \mathbf{u} nor \mathbf{D} depends on \mathbf{n} and ∇ is with respect to local coordinates,

$$\frac{\partial}{\partial t} \left(\sum_{\mathbf{n}} c(\mathbf{n}, \mathbf{x}, t) \right) + \nabla \cdot \left(\mathbf{u} \sum_{\mathbf{n}} c(\mathbf{n}, \mathbf{x}, t) \right) - \nabla \cdot \left(\mathbf{D} \nabla \sum_{\mathbf{n}} c(\mathbf{n}, \mathbf{x}, t) \right) = 0 \quad (33)$$

or

$$\frac{\partial a}{\partial t} + \nabla \cdot (\mathbf{u}a) - \nabla \cdot (\mathbf{D}\nabla a) = 0 \quad (34)$$

$a(\mathbf{x}, t)$ satisfies partial differential equation (34) and the following boundary conditions:

$$a(l_1/2, x_2, x_3, t) = a(-l_1/2, x_2, x_3, t) \quad (35)$$

$$a(x_1, l_2/2, x_3, t) = a(x_1, -l_2/2, x_3, t) \quad (36)$$

$$a(x_1, x_2, l_3/2, t) = a(x_1, x_2, -l_3/2, t) \quad (37)$$

$$\frac{\partial a}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} = \frac{\partial a}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} \quad (38)$$

$$\frac{\partial a}{\partial x_i} \Big|_{x_1, l_2/2, x_3, t} = \frac{\partial a}{\partial x_i} \Big|_{x_1, -l_2/2, x_3, t} \quad (39)$$

and

$$\frac{\partial a}{\partial x_i} \Big|_{x_1, x_2, l_3/2, t} = \frac{\partial a}{\partial x_i} \Big|_{x_1, x_2, -l_3/2, t} \quad (40)$$

where $i = 1, 2, 3$. These conditions are obtained through summation over \mathbf{n} . Proofs are given in Appendix A.

To determine the equation satisfied by the components of the first local moment, we follow a similar procedure. For the first component, we find that b_1 satisfies exactly the same form of a differential equation as a :

$$\frac{\partial b_1}{\partial t} + \nabla \cdot (\mathbf{u}b_1) - \nabla \cdot (\nabla b_1) = 0 \quad (41)$$

but with different boundary conditions:

$$b_1(l_1/2, x_2, x_3, t) = b_1(-l_1/2, x_2, x_3, t) - a(-l_1/2, x_2, x_3, t)l_1 \quad (42)$$

$$b_1(x_1, l_2/2, x_3, t) = b_1(x_1, -l_2/2, x_3, t) \quad (43)$$

$$b_1(x_1, x_2, l_3/2, t) = b_1(x_1, x_2, -l_3/2, t) \quad (44)$$

$$\frac{\partial b_1}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} = \frac{\partial b_1}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} - \frac{\partial a}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} l_1 \quad (45)$$

$$\frac{\partial b_1}{\partial x_i} \Big|_{x_1, l_2/2, x_3, t} = \frac{\partial b_1}{\partial x_i} \Big|_{x_1, -l_2/2, x_3, t} \quad (46)$$

$$\frac{\partial b_1}{\partial x_i} \Big|_{x_1, x_2, l_3/2, t} = \frac{\partial b_1}{\partial x_i} \Big|_{x_1 x_2, -l_3/2, t} \quad (47)$$

By analogy, the partial differential equation and the boundary conditions which must be satisfied by b_2 and b_3 can be obtained.

Now consider the second local moment. Each of its elements, C_{ij} , satisfies

$$\frac{\partial C_{ij}}{\partial t} + \nabla \cdot (u C_{ij}) - \nabla \cdot (\nabla C_{ij}) = 0 \quad (48)$$

with given boundary conditions. Consider, first, the case of C_{11} .

$$C_{11}(l_1/2, x_2, x_3, t) = C_{11}(-l_1/2, x_2, x_3, t) - 2b_1(-l_1/2, x_2, x_3, t)l_1 + a(-l_1/2, x_2, x_3, t)l_1^2 \quad (49)$$

$$C_{11}(x_1, l_2/2, x_3, t) = C_{11}(x_1, -l_2/2, x_3, t) \quad (50)$$

$$C_{11}(x_1, x_2, l_3/2, t) = C_{11}(x_1, x_2, -l_3/2, t) \quad (51)$$

$$\frac{\partial C_{11}}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} = \frac{\partial C_{11}}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} - 2 \frac{\partial b_1}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} l_1 + \frac{\partial a}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} l_1^2 \quad (52)$$

$$\frac{\partial C_{11}}{\partial x_i} \Big|_{x_1, l_2/2, x_3, t} = \frac{\partial C_{11}}{\partial x_i} \Big|_{x_1, -l_2/2, x_3, t} \quad (53)$$

$$\frac{\partial C_{11}}{\partial x_i} \Big|_{x_1, x_2, l_3/2, t} = \frac{\partial C_{11}}{\partial x_i} \Big|_{x_1, x_2, -l_3/2, t} \quad (54)$$

By analogy, we obtain the boundary value problems for the other diagonal elements.

The boundary conditions for C_{12} are:

$$C_{12}(l_1/2, x_2, x_3, t) = C_{12}(-l_1/2, x_2, x_3, t) - b_2(-l_1/2, x_2, x_3, t)l_1 \quad (55)$$

$$C_{12}(x_1, l_2/2, x_3, t) = C_{12}(x_1, -l_2/2, x_3, t) - b_1(x_1, -l_2/2, x_3, t)l_2 \quad (56)$$

$$C_{12}(x_1, x_2, l_3/2, t) = C_{12}(x_1, x_2, -l_3/2, t) \quad (57)$$

$$\frac{\partial C_{12}}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} = \frac{\partial C_{12}}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} - \frac{\partial b_2}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} l_1 \quad (58)$$

$$\frac{\partial C_{12}}{\partial x_i} \Big|_{x_1, l_2/2, x_3, t} = \frac{\partial C_{12}}{\partial x_i} \Big|_{x_1, -l_2/2, x_3, t} - \frac{\partial b_1}{\partial x_i} \Big|_{x_1, -l_2/2, x_3, t} l_2 \quad (59)$$

$$\frac{\partial C_{12}}{\partial x_i} \Big|_{x_1, x_2, l_3/2, t} = \frac{\partial C_{12}}{\partial x_i} \Big|_{x_1, x_2, -l_3/2, t} \quad (60)$$

Similarly for all other off-diagonal elements of the second-moment tensor C .

5 Equations for rates of change of the global moments

From Equation (34)

$$\int_V \left\{ \frac{\partial a}{\partial t} + \nabla \cdot (\mathbf{u}a) - \nabla \cdot (\mathbf{D}\nabla a) \right\} dx = 0 \quad (61)$$

Integrating each term and using the divergence theorem,

$$\frac{d\alpha}{dt} = \int_V \nabla \cdot [-\nabla a + (\nabla a)] dx = \int_S [-\mathbf{u}a + (\nabla a)] \cdot \boldsymbol{\eta} dS \quad (62)$$

where S is the surface which surrounds the parallelepipedal element, $\boldsymbol{\eta}$ is a unit vector normal to the surface and pointed outward, and dS is an infinitesimal area on the surface which surrounds the element. Because of symmetry in $\mathbf{u}(\mathbf{x})$, \mathbf{D} , $a(\mathbf{x}, t)$, and ∇a on the boundary, this integral vanishes and we obtain that

$$\frac{d\alpha}{dt} = 0 \quad (63)$$

This result was anticipated since, according to Equation (11), no mass is added to or subtracted from the system after the initial time.

In a similar fashion, the rate of increase of β_1 , the first element of the first moment, is

$$\begin{aligned} \frac{d\beta_1}{dt} &= \int_S [-(\mathbf{u}b_1) + (\mathbf{D}\nabla b_1)] \cdot \boldsymbol{\eta} dS \\ &= \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [-u_1(-l_1/2, x_2, x_3) \{b_1(l_1/2, x_2, x_3, t) \\ &\quad - b_1(-l_1/2, x_2, x_3, t)\} + \sum_{i=1}^3 D_{1i} \left\{ \frac{\partial b_1}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} - \frac{\partial b_1}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} \right\}] dx_2 dx_3 \\ &= l_1 \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [u_1(-l_1/2, x_2, x_3) a(-l_1/2, x_2, x_3, t) - \mathbf{d}_1 \cdot \nabla a|_{-l_1/2, x_2, x_3, t}] dx_2 dx_3 \quad (64) \end{aligned}$$

where \mathbf{d}_1 is the vector formed by the first column of the microdispersion tensor \mathbf{D} . Note that \mathbf{D} is symmetric.

Similarly for the other components:

$$\frac{d\beta_2}{dt} = l_2 \int_{-l_1/2}^{l_1/2} \int_{-l_3/2}^{l_3/2} [u_2(x_1, -l_2/2, x_3) a(x_1, -l_2/2, x_3) - \mathbf{d}_2 \cdot \nabla a|_{x_1, -l_2/2, x_3, t}] dx_1 dx_3 \quad (65)$$

and

$$\frac{d\beta_3}{dt} = l_3 \int_{-l_1/2}^{l_1/2} \int_{-l_2/2}^{l_2/2} [u_3(x_1, x_2, -l_3/2) a(x_1, x_2, -l_3/2) - \mathbf{d}_3 \cdot \nabla a|_{x_1, x_2, -l_3/2, t}] dx_1 dx_2 \quad (66)$$

What is particularly interesting is that the rate of increase of the first global moment depends only on the zero local moment. The same is true in the analysis of the problem examined in the classical works of Taylor (1953) and Aris (1956).

Consider now the second moment. The rate of increase of Γ_{11} is

$$\begin{aligned} \frac{d\Gamma_{11}}{dt} &= \int_S [-(\mathbf{u}C_{11}) + (\nabla C_{11})] \cdot \boldsymbol{\eta} dS \\ &= \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [-u_1(-l_1/2, x_2, x_3) \{C_{11}(l_1/2, x_2, x_3, t) - C_{11}(-l_1/2, x_2, x_3, t)\}] \end{aligned}$$

$$\begin{aligned}
& + \sum_{i=1}^3 D_{1i} \left\{ \frac{\partial C_{11}}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} - \frac{\partial C_{11}}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} \right\} dx_2 dx_3 \\
& = \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} \{ u_1(-l_1/2, x_2, x_3) \{ 2l_1 b_1(-l_1/2, x_2, x_3, t) - l_1^2 a(-l_1/2, x_2, x_3, t) \} \\
& + d_1 \cdot \nabla(-2b_1 l_1 + a l_1^2) \Big|_{-l_1/2, x_2, x_3, t} \} dx_2 dx_3 \tag{67}
\end{aligned}$$

For rate of increase of Γ_{12}

$$\begin{aligned}
\frac{d\Gamma_{12}}{dt} & = \int_S [-(u C_{12}) + (\mathbf{D} \nabla C_{12})] \cdot \boldsymbol{\eta} dS \\
& = \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [-u_1(-l_1/2, x_2, x_3) \{ C_{12}(l_1/2, x_2, x_3, t) - C_{12}(-l_1/2, x_2, x_3, t) \} \\
& + \sum_{i=1}^3 D_{1i} \left\{ \frac{\partial C_{12}}{\partial x_i} \Big|_{l_1/2, x_2, x_3, t} - \frac{\partial C_{12}}{\partial x_i} \Big|_{-l_1/2, x_2, x_3, t} \right\} dx_2 dx_3 \\
& + \int_{-l_1/2}^{l_1/2} \int_{-l_3/2}^{l_3/2} [-u_2(x_1, -l_2/2, x_3) \{ C_{12}(x_1, l_2/2, x_3, t) - C_{12}(x_1, -l_2/2, x_3, t) \} \\
& + \sum_{i=1}^3 D_{2i} \left\{ \frac{\partial C_{12}}{\partial x_i} \Big|_{x_1, l_2/2, x_3, t} - \frac{\partial C_{12}}{\partial x_i} \Big|_{x_1, -l_2/2, x_3, t} \right\} dx_1 dx_3 \\
& = \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [u_1(-l_1/2, x_2, x_3) l_1 b_2(-l_1/2, x_2, x_3, t) - l_1 d_1 \cdot \nabla b_2 \Big|_{-l_1/2, x_2, x_3, t}] dx_2 dx_3 \\
& + \int_{-l_1/2}^{l_1/2} \int_{-l_3/2}^{l_3/2} [u_2(x_1, -l_2/2, x_3) l_2 b_1(x_1, -l_2/2, x_3, t) - l_2 d_2 \cdot \nabla b_1 \Big|_{x_1, -l_2/2, x_3, t}] dx_1 dx_3 \tag{68}
\end{aligned}$$

In a similar fashion, we obtain the equations for all other elements.

6 Large-time behavior

As the solute plume spreads, the distribution $a(\mathbf{x}, t)$ gradually becomes more uniform as the tagged particle becomes equally likely to be at any point in the *phase space* which, in our case, is defined as a representative elementary volume. (We use the term "phase space" for two reasons. First, to underline its difference from the unbounded geometric space which contains the particles. Second, to point out that the elementary volume plays a role similar to the phase space of statistical mechanics. Of course, in the classical approximation in statistical mechanics the phase space is defined as the cartesian multidimensional space whose axes are labeled by all the coordinates and momenta describing the system (Reif, 1967, p. 256). For the problem at hand, however, the momentum of a particle is not needed. J. H. Cushman (personal communication) disagreed with the use of the term "phase space" in this context and suggested the use of the term "configuration space.")

One may indeed verify that the steady-state solution to the boundary value problem of Eqs (34) through (40) is

$$a(\mathbf{x}, t) = \frac{1}{l_1 l_2 l_3} \tag{69}$$

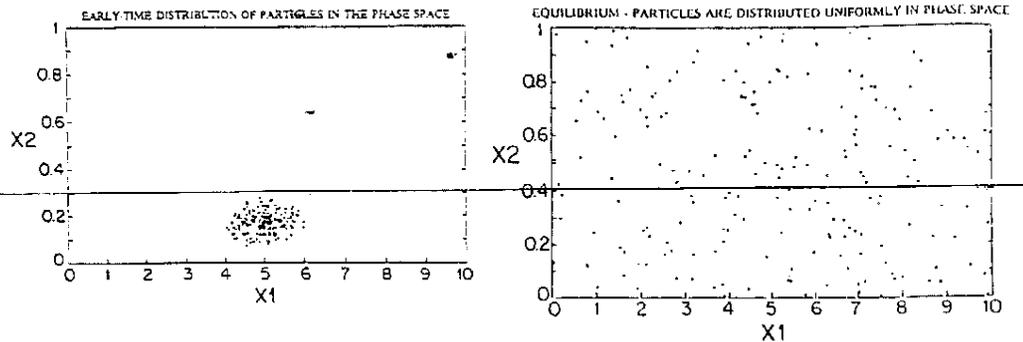


Figure 3. (a) Example of the pre-asymptotic distribution of 200 solute particles in the phase space. (b) The distribution of 200 particles in the phase space at a large time (Equilibrium)

which means that \mathbf{x} , the local coordinate of the location occupied by a market particle, is uniformly distributed. Note that this solution might not be necessarily valid if the condition $\nabla \cdot \mathbf{u} = 0$ were not satisfied.

One way to visualize the meaning of equations (34)-(40) is by considering the movement of a tagged particle within the box that we called the phase space. This particle moves with advective velocity $\mathbf{u}(\mathbf{x})$ and is subjected to random Brownian motion with dispersion tensor $\mathbf{D}(\mathbf{x})$, where \mathbf{x} is the location of the particle in the box (which coincides with the local coordinate of the particle as it moves in space.) What is interesting about the box is that a particle which passes through the wall at a certain point immediately reappears on the opposite wall! (See Figure 2.) Thus, the system can be described as *closed* (Kitter and Kroemer, 1980, p. 29) or *isolated* (Reif, 1967, p. 50) with no mass being gained or lost to the surroundings.

Even if at time t_0 most of the particles are found congregated around a point within the box (Figure 3a), given enough time these particles will spread out within the box so that the distribution of the particles will become approximately uniform (Figure 3b), the maximum-entropy distribution for the phase space. When this happens, we say that the system is in *equilibrium*. Taylor (1953) postulated for a similar problem that equilibrium will be reached independently of the initial condition; the work of Aris (1956) confirmed that the assumption was correct by formally computing the zero local moment.

It is of great practical importance to compute the *relaxation time* which needs to elapse before equilibrium is reached. This can be computed by solving (34)-(40) with initial condition a unit-mass point injection and determining the time that is needed for $a(\mathbf{x}, t)$ to become approximately uniform. Nevertheless, a rough estimate of the relaxation time can be obtained from a simple argument (Taylor, 1953, Chatwin, 1970). The relaxation time is the time it takes a marked particle to diffuse throughout the length of the box which is approximately l^2/D , where l is the size of the box and D is the local dispersion coefficient. Thus, the local dispersion coefficient is a critical factor in determining the relaxation time required for the asymptotic results to become valid. Indeed, even when D does not appreciably affect the value of macrodispersion coefficients, as shown correctly for large Peclet numbers and small variances in the works of Gelhar and Axness (1983), Dagan (1984), and Neuman et al. (1987), there is no escaping the fact that it may decide whether the large time results are applicable

or not. Without local dispersion, it is questionable whether equilibrium is reached or maintained and the transport of a given plume at finite times cannot be easily predicted from macroscopic transport coefficients, as indicated in the simulations of Smith and Schwarz (1980). They found that the effective dispersion coefficients in a given formation varies erratically with time and is very sensitive to small changes in the local arrangement of conductivity elements (the "microstructure".)

Even though the relaxation time needed for the asymptotic result to be valid can be long, these results are applicable at early times as predictions with incomplete information. In statistical mechanics, Jaynes (1985) has vigorously argued that such upscaling methods should be regarded "as representing, not mechanical prediction from the equations of motion, but only the process of inference (make the best predictions you can from the information you have) ..." (ibid., p. 25). Thus, even if the asymptotic domain has not been reached, the asymptotic results (velocity and marodispersion) are the best predictions possible in the absense of information about the location and size of the plume. In this case, it is appropriate to assume that the location of a tagged particle in the phase space is uniformly distributed not because enough time has elapsed but because this distribution expresses our state of uncertainty about the location of this particle. However, better predictions may be obtained which use additional information.

Once $a(\mathbf{x}, t)$ is determined, we can calculate the rate of change of β

$$\frac{d\beta_1}{dt} = \frac{1}{l_2 l_3} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} u_1(-l_1/2, x_2, x_3) dx_2 dx_3 = \bar{u}_1 \quad (70)$$

and analogous relations for $\frac{d\beta_2}{dt}$ and $\frac{d\beta_3}{dt}$.

Thus the centroid of the plume moves with the (spatially) average velocity:

$$\mathbf{u}^m = \frac{d\beta}{dt} = \frac{1}{l_1 l_2 l_3} \int_V \mathbf{u}(\mathbf{x}) d\mathbf{x} \quad (71)$$

The first local moment can now be determined from the solution of a boundary value problem, Equations (41) through (47). Starting with b_1 , one may verify that at large times

$$b_1(x_1, x_2, x_3, t) = \{Constant + \bar{u}_1 t - x_1 + g_1(x_1, x_2, x_3)\} / l_1 l_2 l_3 \quad (72)$$

Then, Equations (41)-(47) simplify as follows:

$$\mathbf{u} \cdot \nabla g_1 - \nabla \cdot (D \nabla g_1) = u'_1 - \nabla \cdot \mathbf{d}_1 \quad (73)$$

subject to the symmetrical boundary conditions:

$$g_1(l_1/2, x_2, x_3) = g_1(-l_1/2, x_2, x_3) \quad (74)$$

$$g_1(x_1, l_2/2, x_3) = g_1(x_1, -l_2/2, x_3) \quad (75)$$

$$g_1(x_1, x_2, l_3/2) = g_1(x_1, x_2, -l_3/2) \quad (76)$$

$$\frac{\partial g_1}{\partial x_1} \Big|_{l_1/2, x_2, x_3} = \frac{\partial g_1}{\partial x_1} \Big|_{-l_1/2, x_2, x_3} \quad (77)$$

$$\frac{\partial g_1}{\partial x_1} \Big|_{x_1, l_2/2, x_3} = \frac{\partial g_1}{\partial x_1} \Big|_{x_1, -l_2/2, x_3} \quad (78)$$

$$\left. \frac{\partial g_1}{\partial x_i} \right|_{x_1, x_2, l_3/2} = \left. \frac{\partial g_1}{\partial x_i} \right|_{x_1, x_2, -l_3/2} \quad (79)$$

In the trivial case that $u'_i(\mathbf{x}) = u_i(\mathbf{x}) - \bar{u}_i$ vanishes and the microdispersion tensor is constant, the solution is obviously $g_1 = 0$. The same is approximately true when the microdispersion dominates in the sense that

$$|D| \gg |u'| \quad (80)$$

Otherwise, the solution depends on the form of the spatially variable velocity and is affected by the mean velocity and the microdispersion coefficients. It can be obtained after integration using analytical or numerical techniques. Such methods are developed elsewhere.

The rate of increase of Γ_{11} may be written as follows:

$$\frac{d\Gamma_{11}}{dt} = 2\bar{u}_1 \int_V b_1 dx + 2 \int_V (u'_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1) dx \quad (81)$$

after substituting areal by volume averages as shown in Appendix B. Then, from the definition of the second central moment and substituting in terms of g_1

$$\begin{aligned} \frac{d\Delta_{11}}{dt} &= 2/l_1 l_2 l_3 \int_V \{u'_1(-x_1 + g_1) - \mathbf{d}_1 \cdot \nabla(-x_1 + g_1)\} dx \\ &= 2/l_1 l_2 l_3 \int_V \{u'_1 g_1 - \mathbf{d}_1 \cdot \nabla g_1\} dx + 2\bar{D}_{11} \end{aligned} \quad (82)$$

where \bar{D}_{11} is the spatial average of D_{11} and we made use of $\int_V u'_1 x_1 dx = 0$ as a consequence of Equation (2).

In general the result is

$$D_{ij}^m = \frac{1}{2} \frac{d\Delta_{ij}}{dt} = \frac{1}{2l_1 l_2 l_3} \int_V \{u'_i g_j - \mathbf{d}_i \cdot \nabla g_j + u'_j g_i - \mathbf{d}_j \cdot \nabla g_i\} dx + \bar{D}_{ij} \quad (83)$$

where D^m is the three-dimensional second-order tensor of macrodispersion.

7 Discussion

The Taylor method for the analysis of dispersion was originally proposed for rectilinear flow in pipes, between plates, or in perfectly stratified media (Taylor, 1953, Aris, 1956, Güven et al., 1984, Hatton and Lightfoot, 1984, and Valocchi, 1989). Taylor (1953) studied the transport of a solute which is injected into a pipe through which a fluid is flowing. He found that the cross-sectional average concentration, which varies along the pipe axis, eventually satisfies an advection-dispersion equation with constant coefficients, which he computed. A landmark in the development of this method was the introduction by Aris (1956) of the method of moments. More recently, the important works of Horn (1971) and particularly Brenner (1980a and 1982a) have pointed out that the basic ideas in Taylor's approach are applicable in a much wider context for the derivation of effective or macroscopic transport coefficients. For example, this generalized Taylor-Aris-Brenner method can deal with the problem of effective conductivity in gradually varying two- or three-dimensional flow in a formation with stationary conductivity (Kitanidis, 1990.)

This work has applied the same approach to determine the macrodispersion coefficients in fully three dimensional flow with seepage velocity and microdispersion coefficients which are periodic in all directions. An important feature of the approach

is the distinction between "local" and "global" moments. The local moments can be determined sequentially solving boundary value problems. First the zero local moment is determined, then the first, and so on. Next, the rate of increase of the n^{th} global moment is found to depend on the first $n-1$ local moments. The first global moment represents the position of the centroid of spatially averaged over one elementary volume (one period) solute concentration and the second moment the spreading (in a mean square sense) of this concentration. The macrodispersion tensor is defined as half the time rate of increase of the second moment.

The key result of this analysis is that the macrodispersion tensor is given by volume averages, equation (83). To compute this expression, one needs to calculate first n auxiliary functions (n = dimension of flow domain), which can be obtained from the solution of n elliptic boundary value problems (Equations 74-80). Note that the microdispersion coefficient not only affects the value of the auxiliary functions but also appears as an additive term in the final result. Most previous works either neglected this term or added it after the analysis was completed.

This derivation did not assume small perturbations, steady state in the concentrations, or linearly varying concentration mean (Gelhar and Axness, 1983). No ensemble averaging is involved in this analysis. The expression is valid for any orientation of the mean velocity.

The results of this analysis are in general agreement with those of Bhattacharya (1985), who followed a completely different method, requiring significantly more advanced mathematics. By contrast, the method of moments required only classical calculus. The present analysis is also more general, accounting for spatial variability in the dispersion coefficients. Furthermore, I believe that there is a difference in the interpretation of the results of the two methods. In the Taylor-Aris-Brenner method we have not attempted to show that the "point" values of concentration, $c(\mathbf{X}, t)$, necessarily satisfy the classical advection-dispersion (AD) equation with constant coefficients. The reason is that at scales smaller than the spatial periodicity, velocity variations tend to distort the concentration distribution in areas with a distribution gradient. (See Frind et al., 1987, who simulated transport in a formation statistically similar to the Borden site, Sudicky, 1986, and Freyberg, 1986.) Thus, at times of interest in applications, I see no reason to believe that the AD with constant coefficients is satisfied by $c(\mathbf{X}, t)$, especially near the edges of the plume. Bhattacharya has focused on very large times and has shown that the concentration c does satisfy the classical AD equation. I believe that this will happen only when so much time has elapsed that all concentration gradients have practically vanished.

This work has focused on \bar{c} , the concentration averaged over one elementary volume or one periodicity cycle. This way, local variability in concentration has been averaged out. However, as the plume spreads over a larger volume, this variability becomes less important and in some applications neglecting it may be justified. The rate of movement of the centroid was found to be equal to the spatial average velocity. Also an expression for the effective dispersion tensor, defined as half the rate of the increase of the spatial covariance was developed.

The conditions which must be met for this result to be valid:

- (i) The velocity must satisfy Equation (2). This is the case for incompressible fluid and practically constant porosity. If this condition is not met, the problem becomes somewhat more complicated because one needs to solve one more differential equation to determine the probability with which a tagged particle samples a velocity. Furthermore, the effective velocity may not be equal to the average velocity.

- (ii) The plume must be spread out enough that all velocities are sampled with the same frequency with which they are encountered in space. Actually, this does not necessarily require that a long period must elapse, unless the initial injection was over a volume much smaller than that of an elementary volume. ~~Furthermore, I have argued that the results are applicable at early times as best predictions in the absence of any information about the location and size of the plume.~~ (Of course, better predictions are generally possible if more information is available. For example: If it is known that the plume is concentrated in a high-velocity part of the flow domain, then the predicted effective velocity should be larger than the one predicted by the asymptotic theory. Also, if the plume is very small in extent and covers an area of relatively uniform flow velocity, the rate of spreading should be smaller than the one predicted by the asymptotic theory.)

When these conditions are satisfied and, at least as far as the first two spatial moments are concerned, the *further evolution* of the spatially averaged concentration may be modeled with the classical advection-dispersion equation with constant coefficients:

$$\frac{\partial \bar{c}}{\partial t} + \mathbf{u}^m \cdot \nabla \bar{c} - \nabla \cdot (\mathbf{D}^m \nabla \bar{c}) = 0 \quad (84)$$

However, it must be noted that Equation (84) may be valid before the plume assumes a Gaussian shape. Chatwin (1970) has argued that at early times after the injection velocity fluctuations tend to distort the plume into an asymmetric shape and Aris (1956) has suggested that skewness introduced at any time lingers on, decaying very slowly. Thus, at the experiment conducted at Borden, Ontario, (Freyberg, 1986) the plume is highly non-Gaussian even after it has spread over many correlation lengths of the velocity fluctuations.

Theoretical analyses based on volume averaging complement stochastic analyses. The former are particularly relevant to the interpretation of the results of field experiments such as the one at Borden. For example, the analysis developed in this paper has shown the need for spatial averaging of measured concentration (before comparing with the predictions of the macrodispersion theory) to remove local-scale variability; and has highlighted the crucial role of local dispersion in determining how quickly the large-time results become valid.

Acknowledgements

This work has been supported by the Office of Research and Development, U. S. EPA, under agreement R-815738-01-0. The content of this article does not necessarily represent the views of the agency.

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Appendix A Boundary conditions for equations satisfied by the local moments

This Appendix describes how the results of Section 4 were obtained.

From (12)

$$\sum_{\mathbf{n}} c(n_1, n_2, n_3, l_1/2, x_2, x_3, t) = \sum_{\mathbf{n}} c(n_1 + 1, n_2, n_3, -l_1/2, x_2, x_3, t) \quad (\text{A.1})$$

we obtain (35). The other boundary conditions for $a(\mathbf{x}, t)$ are obtained in similar fashion.

From equation (11)

$$\sum_{\mathbf{n}} \frac{\partial c}{\partial t} + \nabla \cdot (uc) - \nabla \cdot (D\nabla c) \mathbf{X}_1(\mathbf{n}) = 0 \quad (\text{A.2})$$

where, $\mathbf{X}_1(\mathbf{n}) = n_1 l_1$. As a consequence, b_1 satisfies exactly the same form of a differential equation as a but with different boundary conditions. From (12)

$$\begin{aligned} \sum_{\mathbf{n}} c(n_1, n_2, n_3, l_1/2, x_2, x_3, t) n_1 l_1 &= \sum_{\mathbf{n}} c(n_1 + 1, n_2, n_3, -l_1/2, x_2, x_3, t) (n_1 + 1) l_1 \\ &- \sum_{\mathbf{n}} c(n_1 + 1, n_2, n_3, -l_1/2, x_2, x_3, t) l_1 \end{aligned} \quad (\text{A.3})$$

so that (42) follows. At the interface which is perpendicular to direction 2:

$$\sum_{\mathbf{n}} c(n_1, n_2, n_3, x_1, l_2/2, x_3, t) n_1 l_1 = \sum_{\mathbf{n}} c(n_1, n_2 + 1, n_3, x_1, -l_2/2, x_3, t) n_1 l_1 \quad (\text{A.4})$$

which is (43). Similarly at the other interface.

Additional boundary conditions for b_1 are obtained from the conditions for the concentration derivatives. From (15):

$$\begin{aligned}
& \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1, n_2, n_3, l_1/2, x_2, x_3, t} n_1 l_1 \\
&= \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t} (n_1+1) l_1 - \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t} l_1 \quad (\text{A.5})
\end{aligned}$$

which is (45). The same procedure can be used at the other two interfaces to find (46) and (47).

Now consider C_{11} . From (12)

$$\begin{aligned}
& \sum_{\mathbf{n}} c(n_1, n_2, n_3, l_1/2, x_2, x_3, t) n_1^2 l_1^2 = \sum_{\mathbf{n}} c(n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t) (n_1+1)^2 l_1^2 \\
& - 2 \sum_{\mathbf{n}} c(n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t) (n_1+1) l_1^2 + \sum_{\mathbf{n}} c(n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t) l_1^2 \quad (\text{A.6})
\end{aligned}$$

which is (49)

At the interface which is perpendicular to direction 2:

$$\sum_{\mathbf{n}} c(n_1, n_2, n_3, x_1, l_2/2, x_3, t) n_1^2 l_1^2 = \sum_{\mathbf{n}} c(n_1, n_2+1, n_3, x_1, -l_2/2, x_3, t) n_1^2 l_1^2 \quad (\text{A.7})$$

Hence (50) and (51).

From (15):

$$\begin{aligned}
& \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1, n_2, n_3, l_1/2, x_2, x_3, t} n_1^2 l_1^2 = \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t} (n_1+1)^2 l_1^2 \\
& - 2 \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t} (n_1+1) l_1^2 + \sum_{\mathbf{n}} \frac{\partial c}{\partial x_i} |_{n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t} l_1^2 \quad (\text{A.8})
\end{aligned}$$

which is Equation (52).

Same procedure at the other interfaces to find (53) and (54). Consider, next, the case of C_{12} . From (12)

$$\begin{aligned}
& \sum_{\mathbf{n}} c(n_1, n_2, n_3, l_1/2, x_2, x_3, t) n_1 l_1 n_2 l_2 \\
&= \sum_{\mathbf{n}} c(n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t) (n_1+1) l_1 n_2 l_2 \\
& - \sum_{\mathbf{n}} c(n_1+1, n_2, n_3, -l_1/2, x_2, x_3, t) l_1 n_2 l_2 \quad (\text{A.9})
\end{aligned}$$

At the interface which is perpendicular to direction 2:

$$\begin{aligned}
& \sum_{\mathbf{n}} c(n_1, n_2, n_3, l_2/2, x_3, t) n_1 l_1 n_2 l_2 = \sum_{\mathbf{n}} c(n_1, n_2+1, n_3, x_1, -l_2/2, x_3, t) n_1 l_1 (n_2+1) l_2 \\
& - \sum_{\mathbf{n}} c(n_1, n_2+1, n_3, x_1, -l_2/2, x_3, t) n_1 l_1 l_2 \quad (\text{A.10})
\end{aligned}$$

At the remaining interface we find the requirement of symmetry. The same procedure with the derivatives.

Appendix B Relation between some surface and volume integrals at large time

From equation (41), apply the divergence theorem over the volume $-l_1/2 \leq x_1 \leq z_1$, $-l_2/2 \leq x_2 \leq l_2/2$, $-l_3/2 \leq x_3 \leq l_3/2$, where $z_1 \leq l_1/2$:

$$\begin{aligned}
& \int_{-l_1/2}^{z_1} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} \frac{\partial b_1}{\partial t} dx_1 dx_2 dx_3 \\
& - \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1)|_{-l_1/2} - (u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1)|_{z_1}] dx_2 dx_3 \\
& = \int_{-l_1/2}^{z_1} \int_{-l_3/2}^{l_3/2} [(u_2 b_1 - \mathbf{d}_2 \cdot \nabla b_1)|_{-l_2/2} - (u_2 b_1 - \mathbf{d}_2 \cdot \nabla b_1)|_{l_2/2}] dx_1 dx_3 \\
& + \int_{-l_1/2}^{z_1} \int_{-l_2/2}^{l_2/2} [(u_3 b_1 - \mathbf{d}_3 \cdot \nabla b_1)|_{-l_3/2} - (u_3 b_1 - \mathbf{d}_3 \cdot \nabla b_1)|_{l_3/2}] dx_1 dx_2 = 0 \tag{B.1}
\end{aligned}$$

because of (43), (44), (46), and (47).

At large times, from Equation (73)

$$\begin{aligned}
& \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1)|_{-l_1/2}] dx_2 dx_3 \\
& = \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1)|_{z_1}] dx_2 dx_3 + \left(\frac{1}{2} + \frac{z_1}{l_1}\right) \tag{B.2}
\end{aligned}$$

Integrating z_1 from $-l_1/2$ to $l_1/2$

$$\begin{aligned}
& l_1 \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1)|_{-l_1/2}] dx_2 dx_3 \\
& = \int_{-l_1/2}^{l_1/2} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1] dx_1 dx_2 dx_3 + \frac{1}{2} l_1 \bar{u}_1 \tag{B.3}
\end{aligned}$$

or

$$\begin{aligned}
& l_1 \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1)|_{z_1}] dx_2 dx_3 \\
& = \int_{-l_1/2}^{l_1/2} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1] dx_1 dx_2 dx_3 - z_1 \bar{u}_1 \tag{B.4}
\end{aligned}$$

which allows the substitution in equation (81) of a surface integral by a volume integral. Similar relations hold for $(u_2 b_2 - \mathbf{d}_2 \cdot \nabla b_2)$ $(u_3 b_3 - \mathbf{d}_3 \cdot \nabla b_3)$.

Now consider

$$\int_{-l_1/2}^{z_1} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} \frac{\partial b_2}{\partial t} dx_1 dx_2 dx_3$$

$$\begin{aligned}
& - \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_2 - \mathbf{d}_1 \cdot \nabla b_2)|_{-l_1/2} - (u_1 b_2 - \mathbf{d}_1 \cdot \nabla b_2)|_{z_1}] dx_2 dx_3 \\
& = \int_{-l_1/2}^{z_1} \int_{-l_3/2}^{l_3/2} [(u_2 b_2 - \mathbf{d}_2 \cdot \nabla b_2)|_{-l_2/2} - (u_2 b_2 - \mathbf{d}_2 \cdot \nabla b_2)|_{l_2/2}] dx_1 dx_3 \\
& + \int_{-l_1/2}^{z_1} \int_{-l_2/2}^{l_2/2} [(u_3 b_2 - \mathbf{d}_3 \cdot \nabla b_2)|_{-l_3/2} - (u_3 b_2 - \mathbf{d}_3 \cdot \nabla b_2)|_{l_3/2}] dx_1 dx_2 \\
& = l_2 \int_{-l_1/2}^{z_1} \int_{-l_3/2}^{l_3/2} [(u_2 a - \mathbf{d}_2 \cdot \nabla a)|_{-l_2/2}] dx_1 dx_3 \tag{B.5}
\end{aligned}$$

At large times, from Equations (69) and (72)

$$\int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_2 - \mathbf{d}_1 \cdot \nabla b_2)|_{-l_1/2}] dx_2 dx_3 = \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_2 - \mathbf{d}_1 \cdot \nabla b_2)|_{z_1}] dx_2 dx_3 \tag{B.6}$$

Integrating z_1 from $-l_1/2$ to $l_1/2$

$$\begin{aligned}
& l_1 \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [(u_1 b_2 - \mathbf{d}_1 \cdot \nabla b_2)|_{-l_1/2}] dx_2 dx_3 \\
& = \int_{-l_1/2}^{l_1/2} \int_{-l_2/2}^{l_2/2} \int_{-l_3/2}^{l_3/2} [u_1 b_1 - \mathbf{d}_1 \cdot \nabla b_1] dx_1 dx_2 dx_3 \tag{B.7}
\end{aligned}$$

which allows the substitution of the surface integral by a volume integral.

Accepted September 30, 1991

