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Pore-scale dilution of conservative solutes: An example

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Abstract. We simulate flow and transport of a conservative nonsorbing tracer in an idealized periodic pore channel using finite element techniques. The concentration is computed; then the slowly varying concentration mean, variance, coefficient of variation, and reactor ratio are calculated through averaging over every cell. The coefficient of variation and reactor ratio are related and quantify the degree of dilution. Then a novel methodology is developed for the evaluation of macroscopic parameters (homogenization), including the variance decay coefficient, which measures the rate with which small-scale concentration fluctuations tend to diminish, and the large-time coefficient of proportionality between the concentration variance and the square of the mean concentration variance. The methodology is based on the solution of a steady advection-dispersion problem in a single cell (which acts as a representative elementary volume); the computed result is then integrated in order to compute the macroscopic parameters. These parameters are compared with the parameters computed through direct simulation on a cell-by-cell basis, and they are found to be in reasonably good agreement. When the macroscopic parameters are used in the macroscopic equations, they produce estimates of the concentration mean and variance that are in agreement with the results of direct simulation.

1. Introduction

Laboratory-scale dispersion of solutes in porous media has been studied extensively (see *Bear* [1972] for review), but the topic remains interesting from a practical and theoretical standpoint [*Mei*, 1992]. The need to understand dilution, mixing, and reactions limited by the rate of diffusion at the pore scale provides new reasons and a new perspective for studying dispersive transport. Also, advances in theories of upscaling (known also as homogenization) and improvements in computational capabilities provide new opportunities for process understanding.

Most research on dispersive transport has focused on the description of the slowly varying mean concentration that is obtained by averaging out microscopic variability. Particular attention has been given to finding the dispersion coefficient that quantifies the rate of spreading of the mean concentration. The literature on the subject is vast, with the books by *Dagan* [1989], *Gelhar* [1993], and *Brenner and Edwards* [1993] providing overviews of selected approaches. Much less attention has been given to the question of small-scale variability about the large-scale mean concentration. How uniform is the concentration at the small scale? This question is related to the important processes of solute dilution and mixing, which cannot be studied solely by a quantification of the rate of spreading of the mean concentration. A solute plume may spread out, but the concentration may vary dramatically at the small scale. The mean concentration does not distinguish between concentration distributions that are uniform at the small scale and those that are patches of high and low concentrations. In hydrogeology this issue has been studied for large-scale transport, and some of these works will be reviewed in section 7.

This study focuses on pore-scale transport of conservative solutes and its scaling up to the laboratory (or Darcy) scale. Through theoretical analysis and numerical simulations, we examine differences between dilution and spreading and how to quantify the evolution of concentration nonuniformity. In order to gain insight into these problems, we will consider an idealized geometry, although the approach is general.

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2. Background

Typically, flow in pores is sufficiently slow and close to solid boundaries for the inertia terms in the Navier-Stokes equations to become negligible compared to viscous and pressure-difference terms. Also, the system reacts to an external impetus fast enough for time derivatives to be neglected. Thus, in the two-dimensional case that will be considered here, the flow satisfies the incompressibility and two momentum-conservation equations, known as the (steady) Stokes equations:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{1}$$

$$g\,\frac{\partial \phi}{\partial x} = \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) \tag{2}$$

$$g\,\frac{\partial \phi}{\partial y} = \nu\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right) \tag{3}$$

where u and v are flow velocities in directions x and y, respectively, ϕ is the hydraulic head, and ν is the kinematic viscosity coefficient. (The dynamic pressure p can be found from the hydraulic head through $p = \rho g \phi$, where ρ is fluid density and g is acceleration of gravity.) The Stokes equations are obtained from the Navier-Stokes equations when the Reynolds number is small. Excellent references on the classic Stokes problem are *Happel and Brenner* [1983], who also provide a historical perspective, and *Pozrikidis* [1992].

These equations are linear, which means that if (u, v, ϕ) is

Table 1. Definition of Dimensionless Variables and Parameters

Dimensionless Variable	Definition
x_d	$x/\bar{w}$
y_d	$y/\bar{w}$
u_d	$u/\bar{u}$
v_d	$v/\bar{u}$
L	$L/\bar{w}$
a_d	$a/\bar{w}$
Pe	$\bar{u}\bar{w}/D$

a solution (i.e., satisfies the governing equations and the no-flux and no-slip conditions on the solid boundaries), then $(au, av, a\phi + b)$ is also a solution for the arbitrary scalars a and b. When the hydraulic-head gradient is multiplied by a factor, the flow velocity is multiplied by the same factor, which leads to Darcy's law: the specific discharge is proportional to the head gradient. In applications we represent groundwater flow at the Darcy scale; that is to say, we replace the porous medium with a continuum where the pore-solid distribution is not resolved and the velocity and head distribution within the pores is averaged.

Consider the transport of a conservative tracer in a steady state velocity field that satisfies the incompressibility condition. The concentration, defined in the liquid phase of the medium, satisfies

$$\frac{\partial c}{\partial t} + u\,\frac{\partial c}{\partial x} + v\,\frac{\partial c}{\partial y} = D\,\frac{\partial^2 c}{\partial x^2} + D\,\frac{\partial^2 c}{\partial y^2} \tag{4}$$

where c is the solute concentration, t is time, and D is the molecular diffusion coefficient.

Velocity fluctuations at the scale of pores cause a swarm of solute particles to spread about their mean position. This spreading is described at the Darcy scale through dispersion coefficients. A dispersion coefficient is defined roughly as one-half the rate of increase of the average square distance of particles from their mean location. Dispersion, particularly in the direction of flow (longitudinal dispersion) that is the focus of this work, has been the subject of considerable experimental and theoretical work. Our emphasis here will be not on dispersion but on small-scale variability of concentration.

Theories of upscaling usually consider media that possess some form of translational invariance (i.e., properties recur in space) such as periodic media and almost periodic media, including stationary random media. Periodic models are particularly popular, such as those given by *Bensoussan et al.* [1978], *Brenner* [1980], and *Mei* [1992]. According to *Mei* [1992, p. 273], "... the periodic model is distinguished by the fact that it can be dealt with most rigorously, without additional heuristic assumptions to simplify the mathematics." Additionally, periodic models are ideal for analyzing the results of numerical experiments because mean values are computed exactly through averaging over one period.

3. Problem Formulation

Consider a channel, formed by a sequence of pores, that is two-dimensional and symmetric about the straight axis [*Dykaar and Kitanidis*, 1996]. The width of the channel is a periodic function:

$$w(x) = \bar{w} + 2a\,\sin\left(2\pi\,\frac{x}{L}\right) \tag{5}$$

where $\bar{w}$ is the average width and $\bar{w} + 2a$ is the maximum width, $a < \bar{w}/2$. The fluid is incompressible, and the flow is steady and periodic. The velocity distribution $u/\bar{u}$, where $\bar{u}$ is the mean velocity, for a given geometry is not dependent on $\bar{u}$. In this work, this velocity distribution will be considered given, computed for a given geometry using a finite element Stokes solver [*Cao and Kitanidis*, 1998a].

Next, render the advection-dispersion equation in dimensionless form by selecting $\bar{w}$ as unit length and $\bar{w}^2/D$ as unit time. The relation between the dimensionless and dimensional quantities is given in Table 1. In practical applications the diffusion coefficient is relatively constant, being of the order of 10^{-9} m^2/s for most chemicals of interest. It is the geometry and the spatial scales of the medium and the groundwater linear velocity that may vary over orders of magnitude. The dimensionless groups of parameters $L/\bar{w}$, $a/\bar{w}$, and Peclet number, $Pe = \bar{u}\bar{w}/D$, may take a wide range of values.

Equations are then rewritten in terms of dimensionless quantities (from this point on the index d will be implied but not explicitly written):

$$w(x) = 1 + 2a\,\sin\left(2\pi\,\frac{x}{L}\right) \tag{6}$$

where $a < 1/2$, and

$$\frac{\partial c}{\partial t} + Pe\,u\,\frac{\partial c}{\partial x} + Pe\,v\,\frac{\partial c}{\partial y} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \tag{7}$$

4. Dispersion and Dilution

Macroscopic descriptions that use Darcy-scale parameters such as the intrinsic permeability and the dispersivity for the prediction of a smoothly varying concentration $\bar{c}$ are undoubtedly valuable. However, in many cases it is important to gain an appreciation for the difference between the smooth $\bar{c}$ described by macroscopic models and the more variable c resolved at the relatively microscopic scale (within a pore, in our case). Large difference indicates incomplete dilution, due to the slow rate of diffusion that allows concentration gradients to be sustained at the small scale. Such gradients can be pronounced in the case of reactive solutes subject to heterogeneous reaction, such as solute transformation in thin biofilms attached to the walls. In the case of conservative solutes, diffusion-controlled gradients are pronounced at the front and back of an advancing solute plume. The gradients are steeper when the Peclet number is large, i.e., when advection is much faster than diffusion.

These points can be illustrated through the following example. Consider the case that $a/\bar{w} = 0.45$ and $L/\bar{w} = 1.5$. The solution to the Stokes problem and the advection dispersion equation was obtained numerically through finite element analysis (the details of the methodology are given by *Cao and Kitanidis* [1998a, b]). The grid used in the flow computations is shown in Figure 1. Only the upper half is shown, the lower half being the mirror image of the upper half. The streamlines are shown in Figure 2. The values of the stream function have been normalized so that the total flow is 1. The streamline that corresponds to stream function value $\Psi = 0$ separates the main-flow zone from a holdup or backwater zone. In the main-flow zone, one eighth of the discharge passes between two

Figure 1. Finite element grid for upper half of unit cell.

consecutive plotted streamlines, as indicated by the values of the stream function shown in Figure 2. It is obvious that most of the flow is concentrated near the center of the pore. In the backwater zone the water rotates slowly compared with the main flow, as indicated by closed streamlines plotted for small differences between the values of the stream function. A solute can cross the line between the main-flow and backwater zones only through diffusion.

Next, consider solute transport. Initially, the concentration is zero everywhere; then, at $t > 0$, the concentration $c = 1$ is imposed at $x = 0$. We will present results for $Pe = 25$ and at (dimensionless) time $t = 1$; this time is sufficiently large, in this case, for the asymptotic results of homogenization theory to be applicable. Figure 3 shows the isoconcentration lines for concentration values from 0 to 1 with intervals of 0.02. In the first six cells the solute is practically fully mixed, and the concentration is ~1 everywhere in the cell. After the 27th cell the concentration remains practically zero, not yet having experienced the influx of mass. The highest concentration gradients in the transverse direction are approximately in the same cells where the gradients are also highest in the longitudinal direction (around the seventeenth cell, appearing as the first cell in the third row in Figure 3). In these cells the mixing is incomplete with considerable differences between the concentration at the walls and at the center of the pore cavity.

For each cell of the periodic medium the mean concentration (at time t) is

Figure 3. Isoconcentration lines for $Pe = 25$.

$$\bar{c} = \frac{1}{V} \int_V c(x, y)\, dV \tag{8}$$

where V is the volume of a cell, which is plotted in Figure 4 as a solid line. (The dashed line is computed from a one-dimensional model using homogenized parameters, as described in section 6.) When dilution or concentration uncertainty is an issue, it is important to supply information about the concentration fluctuation about the mean,

$$c' = c - \bar{c} \tag{9}$$

Figure 2. Streamlines for upper half of unit cell.

Figure 4. Concentration mean: direct simulation (solid line) and analytic solution (dashed line).

Figure 5. Concentration variance: direct simulation (solid line) and analytic solution (dashed line).

Concentration variability within the cell may be quantified through the concentration variance,

$$\sigma_c^2 = \frac{1}{V}\int_V (c'(x, y))^2\, dV \tag{10}$$

For the computation of volume averages of concentration fluctuations, the mean concentration within a cell is approximated by a linear function of x, i.e., within cell i,

$$c'(x, y) = c(x, y) - \bar{c}_i - (\bar{c}_{i+1} - \bar{c}_{i-1})\frac{x - \bar{x}_i}{2L} \tag{11}$$

where $\bar{c}_i$ is the concentration mean in cell i and $\bar{x}_i$ is the coordinate of the center of cell i.

The concentration coefficient of variation is defined as

$$C_V = \frac{\sigma_c}{\bar{c}} \tag{12}$$

The coefficient of variation is a measure of the relative nonuniformity of the concentration within a cell (small-scale variability), and it is directly related to the degree of dilution within a cell [*Kapoor and Kitanidis*, 1996]: the smaller the C_V, the more complete the dilution within the cell. As seen in Figures 4–6, $\bar{c}$, σ_c^2, and C_V vary slowly in the longitudinal dimension, as is expected from mean quantities. The maximum concentration variance is where the mean concentration has the steepest gradient. The coefficient of variation increases toward the front edge of the plume, where the chemical had the least time to dilute.

Another measure of variability or dilution is given through a reactor ratio [*Kitanidis*, 1994]. Here we will define a reactor ratio for each cell, an approach that differs from the approach of *Kitanidis* [1994]. In an intuitive sense, the reactor ratio is the ratio of effective volume occupied by the solute in a pore to the total pore volume. Values of M near 1 indicate complete dilution whereas values near 0 indicate that the solute mass is nonuniformly distributed within the pore. Noting that the total mass within each cell is $\bar{c}V$, the reactor ratio in each cell is

$$M = \frac{1}{V}\exp\left[-\int_V \frac{c(x, y)}{\bar{c}V}\ln\left(\frac{c(x, y)}{\bar{c}V}\right) dV\right] \tag{13}$$

which, for the case at hand, can be written as

$$M = \exp\left[-\frac{1}{V}\int_V \frac{c(x, y)}{\bar{c}}\ln\left(\frac{c(x, y)}{\bar{c}}\right) dV\right] \tag{14}$$

M is computed over every cell, and its values are plotted in Figure 7. It is practically 1 in the first 10 cells and decreases toward the front end of the plume. Both C_V and M suggest that the dilution is poor at the front of the breakthrough curve.

Kapoor and Kitanidis [1996] developed an approximate relation between the coefficient of variation and the reactor ratio based on a low-order expansion. Adapting their approach,

$$\frac{c}{\bar{c}}\ln\left(\frac{c}{\bar{c}}\right) = \frac{\bar{c} + c'}{\bar{c}}\ln\left(\frac{\bar{c} + c'}{\bar{c}}\right) \approx \frac{c'}{\bar{c}} + \frac{1}{2}\left(\frac{c'}{\bar{c}}\right)^2 \tag{15}$$

which is a reasonable approximation when $|c'/\bar{c}| \ll 1$. Then

$$M \approx \exp\left[-\frac{C_V^2}{2}\right] \tag{16}$$

This relation is reasonably accurate, as Figure 7 indicates, because the coefficient of variation is small in our example.

5. Macroscopic Description

In hydrogeologic practice, it is not possible and usually not necessary to obtain a detailed pore-scale description of flow

Figure 6. Concentration coefficient of variation from direct simulation.

Figure 7. Concentration reactor ratio from direct simulation (solid line) and estimate from coefficient of variation (dashed line).

Figure 8. Estimate of the rate of dispersive transport from direct simulation.

and transport over large regions. The common approach is to work with a slowly variable (mean) concentration. It is known that the mean concentration for the problem at hand satisfies the advection-dispersion equation with constant coefficients,

$$\frac{\partial \bar{c}}{\partial t} + Pe\,\frac{\partial \bar{c}}{\partial x} - \bar{D}\,\frac{\partial^2 \bar{c}}{\partial x^2} = 0 \tag{17}$$

where Pe is the mean velocity (in nondimensional terms) and $\bar{D}$ is the dispersion coefficient (which can be much larger than the molecular diffusion coefficient, which is 1 after nondimensionalization). The dispersion coefficient measures the correlation between velocity and concentration fluctuations. An estimate of the dispersion coefficient in each cell can be computed as follows:

$$\bar{D} = \left(\frac{1}{-\dfrac{\partial \bar{c}}{\partial x}}\right)\frac{1}{V}\int_V \left[Pe\,u'c' - \frac{\partial c'}{\partial x}\right] dV + 1 \tag{18}$$

$$= \left(\frac{1}{-\dfrac{\partial \bar{c}}{\partial x}}\right)\frac{1}{V}\int_V \left[\left(\frac{\partial c}{\partial x}\right)^2 + \left(\frac{\partial c}{\partial y}\right)^2\right] dV \tag{19}$$

It is emphasized that this is just an estimate computed under the assumption of periodic boundary conditions of concentration within every cell (see Appendix). In reality, the periodicity condition becomes valid only at very large times, and our approximation affects the estimate of macroscopic parameters. Additionally, there are numerical errors associated with the direct simulation of small-scale concentration fluctuations. Note that the estimated $\bar{D}$ depends on derivatives of concentration and thus is affected by errors in computing small-scale concentration fluctuations. Nevertheless, the estimates are indicative of the rates of dispersive transport at a point in time. The estimates are plotted in Figure 8. The estimates of $\bar{D}$ vary from cell to cell, but these differences diminish slowly as time passes, and the mass spreads over many cells. Note that values of $\bar{D}$ cannot be computed through direct simulation in cells where the gradient of the mean concentration is practically zero.

Equation (17) has attracted most of the attention in upscaling and has been derived through many different methods. However, anyone interested in dilution or concentration uncertainty should evaluate the concentration variance. According to the theory of *Kapoor and Gelhar* [1994a, b], the concentration variance satisfies

$$\frac{\partial \sigma_c^2}{\partial t} + Pe\,\frac{\partial \sigma_c^2}{\partial x} - \bar{D}\,\frac{\partial^2 \sigma_c^2}{\partial x^2} = 2(\bar{D} - 1)\left(\frac{\partial \bar{c}}{\partial x}\right)^2 - \frac{2}{V}\int_V \left(\left(\frac{\partial c'}{\partial x}\right)^2 + \left(\frac{\partial c'}{\partial y}\right)^2 + 2\,\frac{\partial c'}{\partial x}\,\frac{\partial c'}{\partial y}\right) dV \tag{20}$$

where the integral indicates averaging over a cell. Equation (20) was obtained by performing ensemble averaging and utilizing closure approximations, such as that the dispersive flux of c'^2 should be Fickian with the same dispersion coefficient as the dispersive flux of $\bar{c}$. Their development was within the context of the small variations of velocity about the mean velocity.

Equation (20) states that σ_c^2 is a scalar quantity that is advected, with the same mean velocity as the mean concentration; dispersed, with dispersion coefficient $\bar{D}$, like the mean concentration; generated owing to the stirring action of variable velocity, represented macroscopically by the product of the dispersion coefficient $\bar{D}$ with the square gradient of the mean concentration; and destroyed owing to the action of diffusion and the presence of small-scale fluctuations of concentration.

Furthermore, *Kapoor and Gelhar* [1994a, b] proposed that the variance decay term is first order, i.e.,

$$-\frac{2}{V}\int_V \left[\left(\frac{\partial c'}{\partial x}\right)^2 + \left(\frac{\partial c'}{\partial y}\right)^2 + 2\,\frac{\partial c'}{\partial x}\,\frac{\partial c'}{\partial y}\right] dV = -\chi\sigma_c^2 \tag{21}$$

They argued that the variance decay coefficient χ is applicable over the whole domain, and they developed an approximate formula that shows the dependence of χ on diffusion and local variability of velocity. This theory was found to be in good agreement with the results of numerical experiments by *Kapoor and Kitanidis* [1996]. However, their formula for determination of χ is not directly applicable here (since they averaged from one Darcy continuum to another more macroscopic Darcy continuum, whereas we average from a liquid-solid medium to a Darcy continuum), and it also assumes small fluctuations of velocity.

Figure 9 plots an estimate of χ in every cell, numerically computed using (21). Note that estimation is not possible at

Figure 9. Estimate of the rate of variance dissipation from direct simulation.

Figure 10. Estimate of the variance coefficient from direct simulation.

the edges, where both the variance and the variance dissipation are almost zero. The estimates of χ in Figure 9 are indicative of the rate of variance dissipation at a certain point in time. Indeed, the inverse of χ represents a characteristic time for the decay of variance, whether or not (21) is strictly valid with a constant χ. One interesting conclusion from Figure 9 is that $\chi \gg 1$, which means that it is considerably higher than if dilution relied only on molecular diffusion. This confirms that even dilution at a single irregular channel is facilitated by the flow, being the result of the interaction of velocity distribution with diffusion. For the case at hand, dilution is enhanced at the necks of the pores where streamlines converge and it is easier for mass to traverse streamlines through diffusion. On the other hand, the boundary between the holdup and main-flow zones can be crossed only through diffusion, which means that the value of the diffusion coefficient does have an impact on the variance decay coefficient.

At sufficiently large times, the last two terms in (20) should dominate [*Vomvoris and Gelhar*, 1990; *Kapoor and Gelhar*, 1994a, b], and thus we may define another macroscopic parameter, the variance coefficient:

$$\alpha = \frac{\sigma_c^2}{(\partial \bar{c}/\partial x)^2} \tag{22}$$

The estimate of α that is numerically computed in every cell is plotted in Figure 10, except at the edges, where α cannot be computed through direct simulation because both the numerator and denominator are zero.

6. Volume Averaging Over a Single Cell

The detailed description of the microscopic concentration c over a large domain is generally computationally impractical, if not infeasible. One of the reasons is that the grid must be fine enough for the grid Peclet number to be $\sim$1. Because of these difficulties, a methodology is needed for computing the macroscopic variables $\bar{c}$ and σ_c^2 without having to compute the microscopic variable c over the whole domain. The concentration mean satisfies (17) and according to the formulation of *Kapoor and Gelhar* [1994a, b], the concentration variance satisfies

$$\frac{\partial \sigma_c^2}{\partial t} + Pe\,\frac{\partial \sigma_c^2}{\partial x} - \bar{D}\,\frac{\partial^2 \sigma_c^2}{\partial x^2} = 2(\bar{D} - 1)\left(\frac{\partial \bar{c}}{\partial x}\right)^2 - \chi \sigma_c^2 \tag{23}$$

Equations (17) and (23) involve three macroscopic variables: the mean velocity $\bar{u}$, the dispersion coefficient $\bar{D}$, and the variance decay coefficient χ. For a periodic medium these macroscopic variables may be computed from a single period, which serves as a representative elementary volume.

The problem can be treated rigorously using the approaches of *Bensoussan et al.* [1978], *Brenner and Edwards* [1993], etc., as, for example, done for macrodispersion by *Kitanidis* [1992]. Here we will opt for a more physical approach based on a representative elementary volume argument, which is explained in the Appendix. However, our approach leads to the same results as the method of moments [*Brenner*, 1980] and the method of multiple scales [*Mei*, 1992], at least for the dispersion coefficient that these works have studied.

In the region where the mean concentration slope varies almost linearly, the distribution of the mass is similar in some sense, as is indicated in Figure 3. This similarity would become easier to see if we were to plot the results as follows: Within every cell, plot $c(x, y) - \bar{c}(x)/|\partial \bar{c}/\partial x|$, which is the concentration minus the average concentration (which should vary linearly over the cell), and normalize by the gradient of the average concentration. The plot thus obtained should be similar from cell to cell. This similarity will be used to introduce a representative elementary volume equal to a single cell subject to unit concentration gradient.

Consider a unit cell and impose a unit mean-concentration gradient plus a time-variant term plus a steady state periodic fluctuation at the two ends. That is,

$$c(0, y) = Pe\,t + L + f(0, y) \qquad x = 0 \tag{24}$$

$$c(L, y) = Pe\,t + f(L, y) \qquad x = L \tag{25}$$

The time-variant term Pet is required because the net advective flux tends to increase the amount of mass stored in the cell and to raise over time the value of concentration within the cell; the $Pe\,t$ term is thus needed in order to maintain a unit average gradient within the cell.

A trial form of solution to the advection-dispersion (7) is then

$$c(x, y, t) = Pe\,t + F(x, y) = Pe\,t + L - x + f(x, y) \tag{26}$$

where f is a periodic function with zero mean. This solution satisfies the boundary conditions. Substituting the trial solution into (7), the governing advection-dispersion equation, and further simplifying it, we obtain

$$Pe\,u\,\frac{\partial F}{\partial x} + Pe\,v\,\frac{\partial F}{\partial y} - \frac{\partial^2 F}{\partial x^2} - \frac{\partial^2 F}{\partial y^2} = -Pe \tag{27}$$

subject to no-flux boundary conditions on the solid boundary and periodic plus unit gradient boundary conditions at the openings of the unit cell. Once this problem is solved and F is known, the deviation from the mean concentration may be computed,

$$f(x, y) = F(x, y) + x - L \tag{28}$$

where f has zero mean volume average.

Thus the problem is reduced to solving a steady advection-dispersion problem over a single unit cell. This problem is solved numerically, but the computational cost is much lower than the cost of solving over many cells a time-variant advection-dispersion problem.

The mean velocity $\bar{u}$ is the spatial average of the velocity

over the unit cell, Pe. The dispersion coefficient $\bar{D}$ is given by computing a volume average over the unit cell:

$$\bar{D} = \frac{1}{V}\int \left[Pe\, u' f - \frac{\partial f}{\partial x} \right] dV + 1$$

$$= \frac{1}{V}\int \left[\left(\frac{\partial F}{\partial x}\right)^2 + \left(\frac{\partial F}{\partial y}\right)^2 \right] dV \tag{29}$$

where V is the volume of the unit cell and $u' = u - 1$ is the velocity fluctuation. The variance decay coefficient of *Kapoor and Gelhar* [1994a, b] should be

$$\chi = \frac{2\,\frac{1}{V}\int \left[\left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2 \right] dV}{\frac{1}{V}\int f^2\, dV} \tag{30}$$

Additionally, the large-time concentration variance should be

$$\alpha = \frac{1}{V}\int f^2\, dV \tag{31}$$

Thus the needed macroscopic variables are found from computations in a single cell and can thus be obtained much more efficiently and accurately than through direct simulation of transport over large domains. The values obtained are $\bar{D} = 22.9$, $\chi = 32.2$, and $\alpha = 1.26$. The differences from the values computed from analysis in each cell must be due to the influence of the source, the finite size of the plume, and numerical errors associated with the direct simulation. Additionally, note that α should be related to the other two coefficients through $\alpha = 2(D - 1)/\chi$; introducing the values of $\bar{D} = 22.9$ and $\chi = 32.2$ into this equation, we obtain $\alpha = 1.36$, a value 8% larger than the independently computed 1.26.

In Figure 4 the concentration mean computed from direct simulation is compared with the concentration computed from the solution to (17), the one-dimensional transport equation, using the parameters obtained from homogenization. The solution is [from *Fried*, 1975, p. 60]

$$\bar{c}(x, t) = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{x - Pe\, t}{2\sqrt{\bar{D}t}}\right) + \exp\left(\frac{Pe\, x}{\bar{D}}\right) \operatorname{erfc}\left(\frac{x + Pe\, t}{2\sqrt{\bar{D}t}}\right) \right] \tag{32}$$

The solution from the homogenization is in good agreement with the solution from the direct simulation, even though the former was computed at a small fraction of the cost of the latter. This confirms that the macroscopic dispersion coefficient $\bar{D}$ was properly computed through homogenization.

In Figure 5 the concentration variance from direct simulation is compared with the concentration variance obtained using (22). In this case, because the variance decays quickly, we expect that the transport of variance should diminish and that the production of variance due to velocity variations should locally balance the decay of variance due to diffusion, hence (22). The agreement between the computed and predicted values is satisfactory.

7. Discussion and Conclusions

It is well known that dilution follows advective-dominated spreading. Small-scale variability in velocity distorts the isoconcentration lines, causing a plume to become less regular; the irregularities then tend to be smoothed through the action of diffusion. In problems where dilution or concentration uncertainty are important, it is not sufficient to find a mean concentration, but it is needed to compute a measure of small-scale variability of concentration, such as the coefficient of variation.

Concentration variability has been studied previously, and a brief review of available methods will be attempted here. Although these works refer to upscaling from a local-scale continuum to a regional-scale continuum, their problem is practically identical with the problem examined in this paper if we make the following substitutions: local dispersion instead of diffusion and macrodispersion instead of dispersion. *Dagan* [1982, 1990] computed the concentration variance following a simple and intuitive Lagrangian approach, which, however, neglected the smoothing effect of local diffusive processes. As a result, this approach tends to overestimate as concentration variance and, a fortiori, the concentration coefficient of variation that is relevant in the description of dilution. *Kabala and Sposito* [1994] also considered cases with zero local dispersion. The approach of *Vomvoris and Gelhar* [1990] predicts that the concentration variance is proportional to the square of the mean concentration; this conclusion appears valid at asymptotically large times. In fact, in the example presented in this work, the concentration variance becomes proportional to the square of the mean-concentration slope quite early, owing to the large rate of variance decay. The approach of *Graham and McLaughlin* [1989] is numerical small perturbation, and it accounts for the decay of variance due to diffusion but does not account for dispersion of variance due to small-scale variability of velocity. A similar approach has been followed by *Neuman* [1993] using an analytic integral-equation methodology.

The crucial issue is to determine the rate of decay of concentration nonuniformity. *Kapoor and Gelhar* [1994a, b] introduced the variance decay coefficient, a macroscopic coefficient. They presented a methodology that leads to an equation that intends to include all important mechanisms (see equation (23)) and that estimates the macroscopic parameters within the context of small-perturbation analysis. That work was extended and related to the problem of dilution by *Kapoor and Kitanidis* [1996].

In this work, we have focused on a concrete example of dilution at the small scale, and we have illustrated through numerical experiments and mathematical analysis the mechanisms that determine dilution and the methods to describe them. We have introduced a novel approach to compute the variance decay coefficient as well as the coefficient of proportionality between the concentration variance and the square of the mean-concentration slope. This approach is not limited by small-variance assumptions but requires the solution of a steady advection-dispersion equation over a single cell, which for a periodic medium serves as a representative elementary volume.

The macroscopic parameters computed from homogenization using the single cell were found to be close to the parameters estimated through averaging of results of direct simulation in a number of cells. The differences are partially justified by approximations made to estimate macroscopic parameters in each cell and by numerical errors in direct simulation. The

results of homogenization were apparently satisfactory because using them in the macroscopic equations yielded good predictions of the concentration mean and variance; these predictions were evaluated by comparison with results obtained through direct simulation of concentration at the pore scale followed by cell averaging. However, finding the macroscopic parameters and solving the macroscopic equations is much more practical than direct simulation of concentration at the microscopic scale.

Appendix

Consider the transport of a conservative solute (an ideal tracer) in the channel, as is shown in Figure 3. Consider part of the tube, volume V, and pose the following problem: Relate the total mass flux in V to the mean velocity and mean concentration gradient. The flux of solute mass may be distinguished into advective and dispersive. One expects that (1) the advective flux is approximately proportional to the mean velocity and (2) the dispersive flux is approximately proportional to the mean concentration gradient, where the coefficient of proportionality defines the dispersion coefficient. For example, the dispersive mass flux generally depends not just on the mean concentration gradient but also on the conditions at the boundary of V. Under certain conditions the effect of the boundary conditions is negligible.

We will take here as V a unit cell of the periodic medium (i.e., a volume between $x = 0$ and $x = L$). The concentration satisfies (4) with periodic velocities u and v and constant D. We will focus on the case that the boundary conditions for concentration on the fluid boundaries are periodic.

Consider the solution

$$c(x, y, t) = -J[\bar{u}t + F(x, y)] + \bar{c} \tag{33}$$

where J is the macroscopic solute concentration gradient ($\partial\bar{c}/\partial x$); $\bar{c}$ is the macroscopic concentration; both J and $\bar{c}$ are considered constant within V; F is steady, satisfies the periodic condition on the fluid boundary,

$$F(0, y) - F(L, y) = L \tag{34}$$

and satisfies the no-flux condition on solid boundaries. Note that the trial solution satisfies all boundary conditions and the governing equation (4) provided that F satisfies

$$u\frac{\partial F}{\partial x} + v\frac{\partial F}{\partial y} - D\frac{\partial^2 F}{\partial x^2} - D\frac{\partial^2 F}{\partial y^2} = -\bar{u} \tag{35}$$

Equation (35) is derived through substitution of trial solution (33) into (4).

Equation (35) is interpreted as an advection-dispersion equation with a uniform distributed sink. Let the flux through the channel be Q. Then net "mass" influx (treating F as a concentration) into the volume through the boundaries is QL, and net mass loss through the distributed sink is $-\bar{u}V$. However, note that $L/\bar{u} = V/Q$ is the mean residence time of water in V. Thus the net influx into V is zero,

$$QL - \bar{u}V = 0 \tag{36}$$

which, by the way, is required for (35) to have a solution.

Notice that solving (35) with its boundary condition specifies F within a constant. It is convenient to select the constant so that we may write

$$F(x, y) = f(x, y) + L - x \tag{37}$$

where the volume average of the fluctuation f is zero.

Consider the flux at any point within V,

$$u(x, y)c(x, y) - D\frac{\partial c}{\partial x} = q_a + q_d \tag{38}$$

where

$$q_a = u(x, y)[\bar{c} - J(\bar{u}t + L - x)] \tag{39}$$

and

$$q_d = -Ju(x, y)f(x, y) + JD\left(\frac{\partial f}{\partial x} - 1\right) \tag{40}$$

The first term, q_a, is advective flux strictly associated with the mean flow because it is unaffected by velocity fluctuations and diffusion. The volume average of q_a is

$$\frac{1}{V}\int\int_V u(x, y)[\bar{c} - J(\bar{u}t + L - x)]\,dx\,dy = \frac{Q}{V}\int_0^L [\bar{c} - J(\bar{u}t + L - x)]\,dx \tag{41}$$

and thus is directly proportional to the discharge.

The second term, q_d, is dispersive flux because it is unaffected by mean velocity but vanishes when there are no velocity fluctuations and the diffusion coefficient is zero. The volume average of the dispersive flux is

$$\frac{1}{V}\int\int_V q_d\,dx\,dy = -\frac{J}{V}\int\int_V u'(x, y)f(x, y)\,dx\,dy + \frac{JD}{V}\int\int_V\left(\frac{\partial f}{\partial x} - 1\right)dx\,dy \tag{42}$$

where u' is the velocity fluctuation from its volume average. Macroscopically, this volume average should be proportional to the macroscopic concentration gradient and a dispersion coefficient $\bar{D}$,

$$\frac{1}{V}\int\int_V q_d\,dx\,dy = -\bar{D}J \tag{43}$$

Thus

$$\bar{D} = \frac{1}{V}\int\int_V u'(x, y)f(x, y)\,dx\,dy - \frac{D}{V}\int\int_V\left(\frac{\partial f}{\partial x} - 1\right)dx\,dy \tag{44}$$

Equation (44) was obtained by considering a unit cell as a representative elementary volume subject to periodic boundary conditions and by performing volume averaging to determine the dispersion coefficient.

The same formula can be obtained using other procedures that give additional insights into the meaning of the results or the conditions for their applicability. The method of moments [*Brenner*, 1980] involves averaging over many cells, leading to periodic boundary conditions. The method of multiple scales [*Mei*, 1992] shows that at large times the microscopic concen-

tration fluctuations tend to become periodic with period L, which is consistent with the results of our direct simulation (see Figure 3). For details on these important methods, see references. The method presented here is more intuitive and simpler to derive than the more formal methods of moments and multiple scales.

The microscopic fluctuations are $-Jf(x, y)$, and thus the concentration variance over the single cell is

$$\sigma_c^2 = J^2 \int \int_V f^2(x, y)\, dx\, dy \tag{45}$$

Similarly, one may compute microscales of *Kapoor and Gelhar* [1994a] to find their variance decay coefficient,

$$\chi = \frac{2\,\dfrac{1}{V} \displaystyle\int \left[\left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2 + 2\,\frac{\partial f}{\partial x}\,\frac{\partial f}{\partial y} \right] dV}{\dfrac{1}{V} \displaystyle\int f^2\, dV} \tag{46}$$

Equations (44)–(46) for the macroscopic parameters may be used for the following purposes: (1) for the determination of macroscopic parameters (i.e., upscaling or homogenization) by solving a steady partial differential equation in a single cell followed by volume averaging and (2) to estimate macroscopic parameters in every cell in the actual transport computed through direct simulation. In this case, f is approximated by actual concentration fluctuation normalized by the mean-concentration gradient, $c'/-(\partial \bar{c}/\partial x)$. The results should be viewed as approximate because these formulae assume periodic boundary conditions for the concentration in every cell, which is not a valid assumption except at very large times after an impetus has been introduced.

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