Concentration fluctuations and dilution in aquifers

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Abstract. The concentration of solute undergoing advection and local dispersion in a random hydraulic conductivity field is analyzed to quantify its variability and dilution. Detailed numerical evaluations of the concentration variance $\sigma^2_c$ are compared to an approximate analytical description, which is based on a characteristic variance residence time (VRT), over which local dispersion destroys concentration fluctuations, and effective dispersion coefficients that quantify solute spreading rates. Key features of the analytical description for a finite size impulse input of solute are (1) initially, the concentration fields become more irregular with time, i.e., coefficient of variation, $CV = \sigma_c/\langle c \rangle$, increases with time ($\langle c \rangle$ being the mean concentration); (2) owing to the action of local dispersion, at large times ($t > VRT$), $\sigma^2_c$ is a linear combination of $\langle c \rangle^2$ and $\left( \partial \langle c \rangle / \partial x \right)^2$, and the CV decreases with time (at the center, $CV \approx (N)^{1/2}$ VRT/$t$, $N$ being the macroscopic dimensionality of the plume); (3) at early time, dilution and spreading can be severely disconnected; however, at large time the volume occupied by solute approaches that apparent from its spatial second moments; and (4) in contrast to the advection–local dispersion case, under advection alone, the CV grows unboundedly with time (at the center, $CV \approx e^{N^2/4}$), and spatial second moment is increasingly disconnected from dilution, as time progresses. The predicted large time evolution of dilution and concentration fluctuation measures is observed in the numerical simulations.

1. Introduction

Intensely monitored field tracer tests reveal irregular spatial distributions of concentrations even in mildly heterogeneous aquifers [e.g., Leblanc et al., 1991]. When the concentration fluctuations are large, the mean concentration $\langle c \rangle$ is an inappropriate quantifier of contaminant exposure. What is the spatial structure of concentration fluctuations? How do they evolve with time? How does the volume occupied by solute, or dilution, relate to the macroscopic dimensions of concentration distributions? These questions are addressed by detailed numerical simulation of flow and advection–local dispersion, and by analyzing the $\sigma^2_c$ budget, for solute transport in a saturated spatially random hydraulic conductivity field subject to a hydraulic gradient.

Geological processes responsible for formation of aquifers result in material with rapidly varying properties. Measurements of hydraulic conductivity of natural porous materials show rapid and intense spatial variations. When such a spatially heterogeneous hydraulic conductivity field, saturated with water, is subjected to a hydraulic gradient, the ensuing flow field reflects the variations in material properties. Solute introduced into such aquifers undergoes spatially varying advection. In addition, the solute undergoes local dispersion ($d_{ij}$ being the local dispersion coefficients) due to pore-scale velocity variations and molecular diffusion. The problem of approximating spatial second moments of the concentration field $\sigma^2_{ij}(t)$ and the mean concentration $\langle c \rangle$ in randomly heterogeneous porous media has received much attention [see Deng and Cashman [1995] and Jaekel and Vereecken [1997] for a comparison of different approaches to theoretically study solute spreading in an aquifer]. When $R_s$ is larger than the empirically inferred hydraulic conductivity correlation scales $\lambda_j$, $R_s$ and $\langle c \rangle$ may be described by effective dispersion coefficients $D_{ij}$, which are typically much larger than the local dispersion coefficients $d_{ij}$. While $\langle c \rangle$ may provide an adequate description of the concentration averaged over spatial volumes much larger than $\lambda_1\lambda_2\lambda_3$, the scales pertinent to assessing contaminant exposure levels (e.g., well screens and the human scale) are typically smaller than that, hence the practical importance of quantifying concentration fluctuations. In contrast to $\langle c \rangle$ and $R_s$, there is no generally accepted description of the spatial-temporal evolution of $\sigma^2_c$ in heterogeneous hydraulic conductivity fields.

Transport models employed to assess field-scale contamination problems can rarely resolve the flow field completely. It is a common and convenient practice to use these models to predict an averaged concentration field by employing effective dispersion coefficients. However, because the exposure to a larger than average toxic concentration may not be mitigated by subsequent exposure to a smaller concentration, understanding the fluctuations of concentration around its averages is central to developing the scientific basis for assessing risk of exposure.

The kinetics of chemical transformations involving multiple species, in the subsurface environment, can be limited by incomplete mixing of the reactants. Quantifying the effect of incomplete mixing on the overall reaction rate requires assessing the correlation between the fluctuations of the concentration of the reactants [Kapoor et al., 1997]. Therefore assessing...
the attenuation of a pollutant due to chemical transformation reactions that occur due to the interaction of the pollutant and other chemical species present in the aquifer also requires understanding concentration fluctuations.

For the pure advection case the relationship of $\sigma_c^2$ with $\langle c \rangle$ is easily understood because $c$ and $c^2$ (and any other power of $c$) are governed by the same hyperbolic equation and their expected values have a similar behavior. However, measurements of concentrations in large-scale tracer tests in aquifers do not exhibit the pure advection feature of an unboundedly increasing CV with time and also exhibit significant dilution with time [Kapoor and Gelhar, 1994b; Thierrin and Kitanidis, 1994]. Therefore the influence of local dispersion on dilution and concentration fluctuations needs to be understood.

In section 2, spatially random hydraulic conductivity and flow fields are described. Concentration fluctuations are determined by detailed numerical simulation in section 3. In section 4 the terms in the $\sigma_c^2$ budget are approximated, and predictions of $\sigma_c^2$ are compared with the results of numerical simulations. The main results of this paper, summarized in section 5, are (1) a description of the spatial temporal behavior of concentration fluctuations in a stationary random media by detailed numerical simulations; (2) a two-parameter closure of the $\sigma_c^2$ budget, which yields simple analytical expressions that describe the numerically observed spatial-temporal structure of concentration fluctuations; and (3) a quantification of the evolution of fluctuation measures and the relationship of the volume occupied by solute to its macroscopic dimensions.

2. Flow in Spatially Random Porous Media

The flux of fluid $q_j$ in the porous continuum (averaged over many pores and solids) follows Darcy’s law, which for the locally isotropic, constant density case is $q_j = -K \frac{\partial \phi}{\partial x_j}$. $K$ is the hydraulic conductivity, and $\phi$ the hydraulic head. The conservation of the incompressible fluid in the incompressible porous continuum requires $\nabla^2 \phi + \nabla \ln K \cdot \nabla \phi = 0$.

2.1. Random Field Representation of Spatially Varying Hydraulic Conductivity

As $K$ is positive and its logarithm appears naturally in the flow problem, $\ln K$ has been represented as a random field in previous studies. Making the decomposition $\ln K = \ln K_G + f$, a description of the hydraulic conductivity up to second statistical moments is made by specifying $K_G$ and the spatial covariance function, $R_{ff}(\xi) = \langle f(x)f(x + \xi) \rangle$, of $f$, the $\ln K$ variations (assumed to be statistically stationary), or its spectrum

$$S_{ff}(k) = (2\pi)^{-m} \int e^{-i k \cdot \xi} R_{ff}(\xi) \ d\xi.$$ Variables with overbars or angle brackets represent ensemble averages. For the sake of illustration, the $m$-dimensional spectrum covariance of $f$ in this study is taken to be

$$S_{ff}(k) = \sigma_f^2 \prod_{i=1}^{m} \frac{2l_i^2 k_i^2}{\pi^2} e^{-k_i^2 l_i^2} = \sigma_f^2 \prod_{i=1}^{m} \left( 1 - \frac{k_i^2 l_i^2}{2l_i^2} \right) e^{-k_i^2 l_i^2}.$$ (1)

where $\sigma_f^2$ is the variance of $\ln K$. At small wave numbers, $S_{ff}$ increases quadratically and achieves its maximum value at $k_i = 1/l_i$ (which is the defining feature of $l_i$) and decreases thereafter, qualitatively similar to some spectra inferred from measurements, e.g., Figure 1 [from Bakr, 1976]. Limitations on the intensity and extent of field sampling severely restrict the range of wave numbers or spatial scales over which the spectrum or covariance can be reliably inferred empirically, which is emphasized by the question marks in Figure 1. The “correlation scale” $l_i$ is referred to the distance along each principal direction at which the covariance falls to $\sigma_f^2 e^{-1}$. For the chosen spectrum, $l_i$ is practically the same as the correlation scale ($l_i = 1.02 l_i$). Figure 2 shows a portion of the simulated two-dimensional slice of the hydraulic conductivity, using the algorithm developed by Dykaar and Kitanidis [1992]. Table 1 lists its properties.

2.2. Divergence-Free Random Flow Spectrum

A description of the seepage velocity $v_j$ (which is the flux divided by the porosity) is needed to examine solute transport. The leading-order solution for the divergence-free spatially varying velocity field ($v_j = v\delta_{ij} + v_j'$) in a multidimensional unbounded domain of porosity $n$, created by a spatially constant mean hydraulic gradient of magnitude $J$ in the $x_1$ direction ($\partial(\phi)/\partial x_1 = -J$), is [Gelhar and Axness, 1983]

$$S_{v_jv_j}(k) = \left( \frac{K_G J}{n} \right)^2 \left( \delta_{ij} - \frac{k_j k_j}{k^2} \right) S_{ff}(k),$$

$$v = \langle v_j \rangle = \frac{K_G J}{n} \left( 1 + \frac{\sigma_f^2}{2} - \int \frac{k_j^2}{k^2} S_{ff}(k) \ dk \right)$$

$$k^2 = \sum_{j=1}^{m} k_j^2 \langle v_j \rangle = 0.$$ (2)

The ensemble averages of the velocity are denoted by $\langle v_j \rangle$, and $v_j'$ represents spatial variations around the ensemble average.

2.3. Numerical Solution

Flow in a realization of the random hydraulic conductivity (Figure 2) is numerically simulated. The difference in the hydraulic head specified at the two longitudinal ends of the hydraulic conductivity field is $J L$, where $L$ is the overall length of the domain. In the simulation, $L = 80 l_2$. The domain extends $100 l_2$ in the vertical, and vertical averages are taken to estimate ensemble averages. No flux occurs through the boundaries at $x_2 = 0$ and $100 l_2$. The hydraulic head solution was
solution algebraic equations resulting from discretization have a unique velocity covariance for perfectly stratified flows. A linearized estimate of the Lagrangian Eulerian counterpart without approximation, except for per-

relate the Lagrangian velocity covariance to its more accessible

Table 1. Hydraulic Conductivity and Flow Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity ( n )</td>
<td>0.3</td>
</tr>
<tr>
<td>( e^{(\ln K)_{\text{eff}}/m} )</td>
<td>100</td>
</tr>
<tr>
<td>Hydraulic gradient magnitude ( J )</td>
<td>0.01</td>
</tr>
<tr>
<td>In K standard deviation ( \sigma_1 )</td>
<td>1.0</td>
</tr>
<tr>
<td>In K correlation scales ( \lambda/l_{\text{avg}} )</td>
<td>51/10.2</td>
</tr>
<tr>
<td>Mean x velocity ( v ), cm/d ( \sigma_{v_1} )</td>
<td>4.7</td>
</tr>
<tr>
<td>Theoretical</td>
<td>4.3</td>
</tr>
<tr>
<td>Velocity standard deviation ( \sigma_{u \nu} ), cm/d ( \sigma_{u \nu} )</td>
<td>4.1/1.0</td>
</tr>
<tr>
<td>Numerical</td>
<td>3.1/0.8</td>
</tr>
<tr>
<td>Theoretical</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Figure 2. Logarithm of simulated hydraulic conductivity field (1/4 of computational domain in each direction): \( l_1 = 50 \) cm, \( l_2 = 10 \) cm, \( \sigma_f = 1 \), and \( K_{\text{eff}} = 100 \) cm/d.

numerically evaluated using a successive overrelaxation finite difference method [Ames, 1992]. The correlation coefficient between the numerically computed \( \partial \nu_i/\partial x_1 \) and \( \partial \nu_j/\partial x_2 \) is \(-0.98\); therefore the numerically computed flow fields are practically divergence free. The numerical scheme converges when \( \Delta x \leq 2/\max (\partial \ln K/\partial x_i) \). This ensures that the set of algebraic equations resulting from discretization have a unique solution [Ames, 1992] and that the hydraulic conductivity field is well resolved. Table 1 lists the properties of the numerically computed flow field, which are close to that implied by the leading-order relationship (2) and (3).

2.4. Lagrangian Integral Timescale

The product of twice the velocity variance and its Lagrangian integral timescale is the asymptotic rate of change of the mean squared displacement of a particle around its mean position [Taylor, 1921]. It is not generally possible to analytically relate the Lagrangian velocity covariance to its more accessible Eulerian counterpart without approximation, except for perfectly stratified flows. A linearized estimate of the Lagrangian velocity covariance \( \langle \nu'_i(P(t))\nu'_j(P(t + \tau)) \rangle \) is often made by replacing a particle’s actual position, \( P(t) \), by its ensemble average, \( \langle v \rangle t \), to get \( \langle \nu'_i(\langle v \rangle t)\nu'_j(\langle v \rangle t + \tau) \rangle \), the Eulerian velocity covariance, which can be evaluated from (2) and (3), where \( \langle v \rangle \) is the mean velocity (in our case, \( \langle v \rangle = (v, 0, 0) \)). For the conductivity field description adopted here (1), such a linearized estimate yields a zero Lagrangian integral timescale (because \( S_f(k) = 0 \) if \( k = 0 \) for any \( i \) and therefore implies an asymptotically zero spreading rate. Without making the linearization (by numerically tracking \( 10^4 \) particles), the Lagrangian integral timescale of the longitudinal velocity component, \( \Lambda^\nu \), was found to be \( O(\sigma_{f1}/v) \), as shown in Figure 3 [Taylor, 1921]:

\[
\Lambda^\nu = (1/\sigma_{v_1}^2) \int_0^\infty \langle \nu'_i(P(t))\nu'_j(P(t + \tau)) \rangle d\tau
\]

\[
= t \rightarrow \infty \frac{1}{(2\sigma_v^2)} \int \partial(P(t) - \tilde{P}(t))^2/\partial t dt
\]

The asymptotic \( x_1 \) effective dispersion coefficient, \( D_{11} = \sigma_{\text{eff}}^2 \Lambda^\nu \), for the pure advection case, is much larger than the local dispersion coefficients employed in the advection–local

Figure 3. Lagrangian integral timescale of the longitudinal velocity \( \Lambda^\nu \). At large time, \( dR^{\nu 2}/dt \rightarrow 2\sigma_v^2 \Lambda^\nu \), where \( R^{\nu 2} \) is the longitudinal spatial second moment. \( \Lambda^\nu \sim O(\sigma_{f1}/v) \) for the three different \( \sigma_f \) analyzed here.
Table 2. Dispersivities and Initial Conditions

<table>
<thead>
<tr>
<th>Case</th>
<th>1*</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local dispersivities $\alpha_L/\alpha_T$, cm</td>
<td>1/1</td>
<td>1/0.5</td>
<td>1/0.25</td>
</tr>
<tr>
<td>Correlation scale local dispersion time $t_d$</td>
<td>10.6</td>
<td>22.1</td>
<td>38.2</td>
</tr>
<tr>
<td>$[2\nu\alpha_T/(\lambda_1)^2 + 2\nu\alpha_L/(\lambda_2)^2]^{-1}$, days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discretization $\Delta x_1/\Delta x_2$, cm</td>
<td>2/2</td>
<td>2/1</td>
<td>2/0.5</td>
</tr>
<tr>
<td>Initial $x_1$ dimensions $R_1(0)/l_1$</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Figure 16 shows the variance residence time for the different cases. * Results for this case are shown in the figures (except for Figures 1, 3, and 17).

dispersion simulations reported in the following sections. This calculation shows that even if $S_{ff}(k) = 0$ for $k_i = 0$ (for any $i$), the random advective heterogeneity can be the dominant cause of spreading for $\sigma_r \sim O(1)$ and can be described by an asymptotically constant effective dispersion coefficient, for the pure advection case. This finding is important because $(1)$ the value of $S_{ff}(k)$ for $k_i = 0$ is difficult to establish from spatial geological data and it is important to understand the effects of the empirical sampling-band-limited spectrum (Figure 1); and $(2)$ in large-scale environmental transport modeling, effective dispersion coefficients are often employed to represent the effects of flow heterogeneity contained in a numerical grid which imposes a low wave number cutoff.

3. Advection–Local Dispersion in Spatially Random Porous Media

The concentration $c$ of solute undergoing advection ($v_i = v/\Delta x_2$ + $v_i$) and local dispersion (with a constant diagonal local dispersion tensor, $d_{ii} = \nu\alpha_i$, $\alpha_{11} = \alpha_L$, $\alpha_{22} = \alpha_T$, $\alpha_{ij} = 0$ if $i \neq j$) follows

$$\frac{\partial c}{\partial t} + \frac{\partial v_i c}{\partial x_i} + \frac{\partial(v_i v_j c)}{\partial x_j} - d_{ij} \frac{\partial^2 c}{\partial x_i \partial x_j} = 0. \quad (4)$$

The concentrations and velocities in this equation are Darcy-scale quantities (i.e., they are averaged over many pores). Laboratory tests have demonstrated that the local dispersivities $\alpha_L$ and $\alpha_T$ are of the order of millimeters. As hydraulic conductivity measurement device dimensions and the porous specimen used to determine local dispersion coefficients are typically much larger than a millimeter, and the spatial measurement interval even larger, the spatial scales of heterogeneity smaller than $\alpha_{ij}$ are not delineated. It follows from (4) that the ensemble mean concentration $\langle c \rangle$ follows

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{\partial v_i \langle c \rangle}{\partial x_i} + \frac{\partial(v_i v_j \langle c \rangle)}{\partial x_j} - d_{ij} \frac{\partial^2 \langle c \rangle}{\partial x_i \partial x_j} = 0. \quad (5)$$

Here $\langle c \rangle$ undergoes mean advection, a macrodispersive flux $\langle c' v_i \rangle$, and a local dispersive flux. Our treatment of $\langle c \rangle$ and $\langle c' v_i \rangle$ is minimal, as our focus is on $\sigma_c^2$.

3.1. Concentration Variance Budget

Subtracting (5) from (4) gives the equation for the concentration perturbation $c' = c - \langle c \rangle$:

$$\frac{\partial c'}{\partial t} + \frac{\partial v_i c'}{\partial x_i} + \frac{\partial(v_i v_j c' - \langle c' v_j \rangle)}{\partial x_j} - d_{ij} \frac{\partial^2 c'}{\partial x_i \partial x_j} = -v_i \frac{\partial \langle v_i \rangle}{\partial x_i}. \quad (6)$$

Multiplying (6) by $c'$ and taking ensemble averages yields the budget for $\sigma_c^2 = \langle c'^2 \rangle$:

$$\frac{\partial \sigma_c^2}{\partial t} + \frac{\partial \sigma_c^2}{\partial x_i} + \frac{\partial(\langle c'^2 \rangle)}{\partial x_i} - d_{ij} \frac{\partial^2 \sigma_c^2}{\partial x_i \partial x_j} = -2\langle v_i \rangle \frac{\partial \langle c \rangle}{\partial x_i} - 2d_{ij} \left( \frac{\partial c'}{\partial x_i} \frac{\partial c'}{\partial x_j} \right). \quad (7)$$

Here $\sigma_c^2$ undergoes transport (mean advection, local dispersion, and a macrodispersive flux $\langle c'^2 v_i \rangle$), like $\langle c \rangle$, and it is produced and destroyed by the forcing on the right-hand side of (7). An overall measure of concentration variability is the spatial integral of the variance,

$$\|\sigma_c^2\| = \int \sigma_c^2 dV,$$

which is called the “global variance.” Integrating (7), assuming homogeneous far-field boundary conditions on $\sigma_c^2$, $\langle c'^2 v_i \rangle$, and $\partial \sigma_c^2/\partial x_i$, gives

$$\frac{\partial \|\sigma_c^2\|}{\partial t} = -2 \left[ \langle c'^2 \rangle \frac{\partial \langle v_i \rangle}{\partial x_i} - 2d_{ij} \left( \frac{\partial c'}{\partial x_i} \frac{\partial c'}{\partial x_j} \right) \right]. \quad (8)$$

In (4)–(8) a sum over repeated indices is implied. For periodic flows, Kapoor and Kitanidis [1996] presented an upper bound on $\|\sigma_c^2\|$ by considering (8) and bounding the variance destruction rate.

The formulation in (4)–(8) and approximate analytical expressions in section 4 are developed for the multidimensional case. The numerical simulations are limited to two-dimensionally heterogeneous media ($m = 2$), in which the ensemble averaged variables vary only in the $x_1$ direction; the numerical simulations are macroscopically one dimensional ($N = 1$). This is effected by introducing solute uniformly over the vertical dimension of the hydraulic conductivity. The initial condition on the concentration is $c(x, 0) = c_p(0) \exp \{-[x_1 - X_1(0)]^2/[2R_1(0)^2]\}$. The initial peak concentration $c_p(0)$ is taken to be 1 unit. $X_1(t)$ is the center of mass of the solute distribution in the $x_1$ direction, and $R_1(t)$ is its radius of gyration in the $x_1$ direction. As the vertical extent of the domain spans $100l_2$, and solute is introduced uniformly over $x_2$, the essential features of the ensemble averages are expected to be contained in the vertical averages. This assertion of ergodicity is verified by conducting flow and transport in independent realizations and showing that the statistics of the concentration fluctuations are not significantly different. In analyzing the numerical simulations, $\|\|$ integrates its argument over $x_1$.

Equation (8) is applicable for the numerical simulation setup because of the stationarity of the concentration field in the $x_2$ direction (the concentration field is nonstationary in the $x_1$ direction). Time is expressed as multiples of $t_d$, the characteristic time of local dispersion over the heterogeneity correlation scales: $t_d = [2\nu\alpha_L(\lambda_1)^2 + 2\nu\alpha_T(\lambda_2)^2]^{-1}$.

3.2. Numerical Discretization

Three advection-dispersion simulations are performed with different transverse dispersivities (Table 2), in addition to the three pure advection simulations performed to infer the Lagrangian integral timescale in section 2. The results of case 1 are shown in Figures 4–15. The concentration field was simulated using a dense-grid ($\Delta x_2 < 2a_{ij}$) centered explicit finite difference scheme [Ames, 1992]. The stringent criteria for stability of the transport solution are adhered to, based on the maximum velocities in each direction. At this level of discreti-
zation, a centered dispersion does not introduce significant numerical dispersion. In addition to constant advection-diffusion solutions, the Townsend [1951] problem was used to check the numerical discretization: an initially Gaussian pulse, subject to diffusion and multidimensional advective compression and elongation,

\[ v_i(x) = v_i(0) + \beta_i x_i \sum_{i=1}^{m} \beta_i = 0 \quad 0 \leq i \leq m, \]

remains Gaussian, with its center of mass at \( X_i(t) = X_i(0) + v_i(0) + \beta_i X_i(0) (e^{\beta_i t} - 1)/\beta_i \) and spatial second moments given by \( R_i^2(t) = R_i^2(0) e^{2\beta_i t} + d_i (e^{2\beta_i t} - 1)/\beta_i \).

Initially, the concentration is uniform over \( x_2 \). Variable advection severely distorts the concentration distribution at early times (Figure 4a, \( X_1(0) = 300 \) cm). The central zone appears to get smooth at large time, \( t \gg t_d \) (Figures 4b–4d). The fringes remain regions of intense variability even at large time. An asymmetry in the concentration distribution is visible at early times, when the plume barely spans a couple of longitudinal correlation scales. The trailing edge appears rounded, and the leading edge appears more incised and irregular. Relatively high concentrations at the trailing edge were found to occur in zones of low hydraulic conductivity; solute is slowly advecting to the trailing edge at early times, when the plume barely spans a couple of longitudinal correlation scales. The trailing edge appears rounded, and the leading edge appears more incised and irregular. Relatively high concentrations at the trailing edge were found to occur in zones of low hydraulic conductivity; solute is slowly exiting these low-conductivity zones due to local dispersion. The relatively high concentration zones in the front are zones of high hydraulic conductivity, into which the fluid is channeling. The numerically determined concentration statistics are presented next. The longitudinal radius of gyration of the solute distribution is shown in Figure 5 [\( R_1(t) \sim t^{1/2} \)] ; \( \langle c \rangle \) and \( \sigma_c \) are shown in Figure 6.

3.3. Concentration Coefficient of Variation CV

Figure 7 shows that the concentration CV, after an initial rise over a few \( t_d \), decreases with time. The overall decrease with time of the CV is shown in Figure 8: the CV plot is flattening out and the CV grows with distance away from the center of mass (Figure 8). This indicates that in the large time limit (\( t \gg t_d \)), the concentration field converges in a spatially nonuniform manner to \( \langle c \rangle \), due to the smoothing action of local dispersion. In section 4, this is explained on the basis of the \( \sigma_c^2 \) budget (7).

The stringent requirement on the grid size (\( \Delta x \ll 2 \sigma_{p_i} \)) (to rule out significant numerical dispersion and correctly model the local dispersive flux) limits the range of local dispersion coefficients explored in this work. However, as the local dispersion coefficients \( d_{ij} \) are less than 2% of the pure advection induced longitudinal effective dispersion coefficient \( D_{11} = \sigma_{c1}^2 \Lambda_{11} \), transport is advection dominated in the simulations.

3.4. Global Variance

The \( \| \sigma_c^2 \| \) exhibits an initial growth and eventual decay (Figure 9). At early times its production rate is larger than the variance destruction rate (8) (Figure 10). Later, the production rate falls below the destruction rate. At large times the dominant balance in the global variance budget (8) is between the production rate and dissipation rate (Figure 10):

\[ \frac{t}{t_d} \gg 1 \quad -2 \left\langle \frac{\partial \langle c \rangle}{\partial x_1} \langle dc' \partial c' \rangle \right\rangle = 2d_{ij} \left\langle \frac{\partial c'}{\partial x_1} \frac{\partial c'}{\partial x_j} \right\rangle, \quad \text{(9)} \]

Figure 9b shows that the inferred \( \| \sigma_c^2 \| \) for two independent realizations of the hydraulic conductivity are not significantly different, i.e., it is possible to infer statistics from one realization for the flow and transport configuration examined here. This is due to the large domain and statistical homogeneity in \( x_2 \).

3.5. Concentration Microscales

The concentration microscales \( \Delta^c_r \) are defined as [Tennekes and Lumley, 1972]

\[ (\Delta^c_r)^2 = \frac{\sigma_c^2}{(\partial c/\partial x_r)^2}. \quad \text{(10)} \]

The concentration microscales initially grow with time (Figure 11a) and later appear to approach a steady state (Figure 11b). The concentration microscales reflect the hydraulic conductivity microstructure, as can be expected for advection-dominated transport. The variations of the microscale over the solute body are not very large.

3.6. Peak Concentration

The peak concentration \( c_p \) can be much larger than the peak of the cross-sectional average concentration \( \langle c \rangle_p \) (Figure 12). Unlike \( c_p \), \( \langle c \rangle_p \sim 1/R_1 \) (Figure 12a). Also, \( c_p \) is not strongly related to \( R_1 \) at early time. Therefore understanding the second moment of a plume at early time does not result in a quantification of dilution. At large times the \( \langle c \rangle_p \) becomes an adequate predictor of \( c_p \) (Figures 12a and 12b). This is consistent with the decrease in the concentration CV with time at large times (Figures 7 and 8). The \( \sigma_c^2 \) provides an upper bound on the exceedance probabilities through Chebyshev’s inequality [Feller, 1968]: the probability that the concentration exceeds the mean by an amount equal to \( \delta \) is always less than or equal to \( \sigma_c^2/\delta^2 \). The addition of a few \( \sigma_c \) to \( \langle c \rangle \) provides an estimate of the peak (Figure 12b). This feature was observed by Kapoor and Gelhar [1994b] for the Cape Cod tracer experiment described by Leblanc et al. [1991].

3.7. Volume Occupied by Solute

An entropy-theoretic measure of volume occupied by solute was formulated by Kitanidis [1994]:

\[ E = \exp \left( -\int_v p \ln p \, dV \right) \quad p = c \int_v c \, dV \quad \text{(11)} \]

Kitanidis referred to \( E \) as the “dilution index” and showed that \( dE/dt = 0 \) when \( d/L = 0 \). This measure helps to quantitatively distinguish between spreading and dilution of solute in heterogeneous flow fields. In our transport problem with solute introduced uniformly over the cross section, \( E_{\text{max}} \) the maximum value of \( E \) for a given \( R_1 \), is attained when the solute is uniformly distributed in the vertical dimension and as a Gaussian in the longitudinal direction. This gives \( E_{\text{max}} = HR_1(t)(2\pi)^{1/2} \) [Kapoor and Kitanidis, 1996]. The actual value of \( E \) can be much less than \( E_{\text{max}} \). The evolution of \( E/E_{\text{max}} \) is shown in Figure 13. The early time rapid decrease is due to the severe advective distortion of the concentration field (Figure 4). The recovery to 1 at large time indicates that eventually the volume occupied by solute can be determined merely by its macroscopic dimensions. Under advection alone, \( E/E_{\text{max}} \) would decrease toward a value of zero at large times as \( R_1(0)/R_1(t) \sim t^{-1/2} \). Note that the time \( E/E_{\text{max}} \) achieves its
Figure 4. Evolution of the concentration field ($l_1 = 50$ cm, $l_2 = 10$ cm; $\alpha_x = 1$ cm, $\alpha_T = 1$ cm; $t_d = [2\nu\alpha_x(\lambda_1)^{-2} + 2\nu\alpha_T(\lambda_2)^{-2}]^{-1}$) showing concentration at (a) $t = 1.1t_d$, (b) $t = 6.5t_d$, (c) $t = 10.4t_d$, and (d) $t = 43.6t_d$. 
minimum value, and the time when the CV and the global variance achieve their maximum values is of the order of $t_d$.

4. Simplified Analytical Description of Concentration Variance and Dilution

Kapoor and Gelhar [1994a, b] obtained an analytical description of $\sigma_c^2$ by approximating the variance budget. That model is briefly stated here and extended to include time-varying constitutive parameters, and compared with the results of detailed numerical simulation.

4.1. Macrodispersive Flux of $c$ and $\sigma_c^2$

Based on a variety of dimensional arguments and detailed analysis, the closure for $\langle c'v'_i \rangle$ is widely taken to be of the Fickian form

$$\langle c'v'_i \rangle = -\nu A_{ij} \frac{\partial \langle c \rangle}{\partial x_j}. \quad (12)$$

Recall that variables within angle brackets are ensemble averages, which are estimated by vertically averaging the numerical results. From our numerical simulation, we are able to assess the longitudinal “macrodispersivity” $A_{11}$ that minimizes

$$\langle (c'v'_1) + \nu A_{11} \frac{\partial \langle c \rangle}{\partial x_1} \rangle. \quad (13)$$

This yields a spatially constant and possibly time varying macrodispersivity (Figure 14). Like $\langle c \rangle$, $\sigma_c^2$ undergoes a macrodispersive flux. For the pure advection case, (12) implies

$$\langle c'^2 \rangle = -\nu \tilde{A}_{ij} \frac{\partial \sigma_c^2}{\partial x_j}.$$

Figure 5. Radius of gyration of plume $R_1$.  

Figure 6. Mean and standard deviation of concentration ($t = 41 t_d$). Solid lines show closure model; symbols, numerical simulation. Here $t_d = [2 \nu \alpha_x (\lambda_1)^{-2} + 2 \nu \alpha_T (\lambda_2)^{-2}]^{-1}$.

Figure 7. Evolution of the coefficient of variation at center of mass. Here $t_d = [2 \nu \alpha_x (\lambda_1)^{-2} + 2 \nu \alpha_T (\lambda_2)^{-2}]^{-1}$; VRT($\infty$) is asymptotic variance residence time.

Figure 8. Spatiotemporal evolution of coefficient of variation. Solid lines show closure model; symbols, numerical simulation. Here $t_d = [2 \nu \alpha_x (\lambda_1)^{-2} + 2 \nu \alpha_T (\lambda_2)^{-2}]^{-1}$. 

with $\tilde{A}_{ij} = A_{ij}$ [Kapoor and Gelhar, 1994a]. Csanady [1973] hypothesized (13) for turbulent transport. In Figure 14 is shown the macrodispersivity $A_{11}$ that minimizes $\| (c'^2) + \nu A_{11} (t) \sigma_c^2 / \partial x_1 \|^2$. $A_{22}$ and $\tilde{A}_{11}$ are close to each other, notwithstanding the influence of local dispersion, as conjectured by Kapoor and Gelhar [1994a] and recently derived by Kapoor and Kitanidis [1997]. Henceforth the same macrodispersivity, $A_{11}$, will be taken to apply to $\langle c \rangle$ and $\sigma_c^2$. In (12) and (13), velocity fluctuations transport $\langle c \rangle$ and $\sigma_c^2$ from where they are large to the regions where they are small, and the rate of transport is proportional to their gradient. The inclusion of the triple product term (13) is one of the main differences between the formulation made in this paper and that of an
earlier study of concentration covariance by Graham and McLaughlin [1989].

### 4.2. Variance Destruction by Local Dispersion

The rate of destruction of concentration variance in (7) is

\[ \xi = 2d_{ij} \left\langle \frac{\partial c'}{\partial x_i} \frac{\partial c'}{\partial x_j} \right\rangle. \]  

(14)

From the definition of concentration microscales (10) and for the diagonal local dispersion tensor employed in this work the variance decay rate is given by

\[ \xi = \chi \sigma_1^2 \quad \chi = \frac{2d_{ij}}{\Delta_i \Delta_j}. \]  

(15)

A sum over repeated subscript indices is implied in (14) and (15). Here \( \chi \) is the “variance decay coefficient.” Its inverse is the characteristic time over which local dispersion destroys concentration variance. This characteristic time is called the “variance residence time,” VRT \( = 1/\chi \). The concentration microscales imply a certain variance decay coefficient \( \chi \) (15). A spatially integrated inference is afforded by \( \chi = \| \xi \| / \| \sigma_1^2 \| \). The initial rise of the VRT (Figure 15) is due to temporally increasing concentration microscales. Sampling larger scale heterogeneity creates larger scales of concentration variability which dissipate slower under the action of local dispersion compared to smaller scales of concentration variability. As the plume dimensions become larger, the macrodispersivities rise with time (Figure 14) and the VRT rises and approaches an asymptotic value (Figure 15). The ratio of the asymptotic VRT and \( t_d \) was found to decrease with a decrease in the transverse local dispersion coefficient (Figure 16), which means that the concentration microscales become smaller when local dispersion coefficients are reduced. As transport becomes increasingly advection dominated (at all scales of variability), the concentration microstructure increasingly reflects the flow microstructure.

Substituting (12), (13), and (15) into (5) and (7) gives

\[ \frac{\partial \langle c \rangle}{\partial t} + v \frac{\partial \langle c \rangle}{\partial x_1} - v(A_i + \alpha_j) \frac{\partial^2 \langle c \rangle}{\partial x_i \partial x_j} = 0, \]  

(16)

\[ \frac{\partial \sigma_1^2}{\partial t} + v \frac{\partial \sigma_1^2}{\partial x_1} - v(A_i + \alpha_j) \frac{\partial^2 \sigma_1^2}{\partial x_i \partial x_j} = 2vA_i \frac{\partial \langle c \rangle}{\partial x_i} \frac{\partial \langle c \rangle}{\partial x_j} - \chi \sigma_1^2. \]  

(17)

A sum over repeated indices is implied in (16) and (17). \( D_{ij} = v(\alpha_i + A_j) \) is the effective dispersion coefficient tensor. For the pure advection case, \( \chi = 0 \) and the effective dispersion

Figure 9a. Evolution of global variance. Solid line shows numerical simulation; dashed line, closure model; \( t_d = [2\nu \alpha_L (\lambda_1)^{-2} + 2\nu \alpha_T (\lambda_2)^{-2}]^{-1} \).

Figure 9b. Evolution of global variance for two independent realizations of hydraulic conductivity.

Figure 10. Evolution of the ratio of rates of destruction and production of variance. Solid line shows numerical simulation; dashed line, closure model; \( t_d = [2\nu \alpha_2 (\lambda_1)^{-2} + 2\nu \alpha_2 (\lambda_2)^{-2}]^{-1} \).

Figure 11a. Concentration microscales showing growth at early time. Here \( t_d = [2\nu \alpha_2 (\lambda_1)^{-2} + 2\nu \alpha_2 (\lambda_2)^{-2}]^{-1} \); \( l_1 = 50 \, \text{cm}, l_2 = 10 \, \text{cm} \).
coefficients are the product of the velocity variance and its Lagrangian integral timescale.

4.3. Relationship With the Classic Pure Advection Result

For the pure advection case in which solute is introduced uniformly over a region at concentration $c_0$, let $f_h(x,t)$ be the probability that a point $x$ at time $t$ is hit by a fluid element carrying the solute at concentration $c_0$, and $[1 - f_h(x,t)]$ the probability that the concentration is 0. Therefore $\langle c \rangle = c_0 f_h$, and $\langle c^2 \rangle = c_0^2 f_h$ and

$$\sigma^2 = \langle c \rangle (c_0 - \langle c \rangle). \quad (18)$$

This classic result was applied by Dagan [1984] to subsurface transport. The formulation leading to (18) assumes nothing about the nature of the flow or source configuration, other than that it applies for the case of uniform source distribution. The expression (18), coupled with the Fickian relation for the macrodispersive flux, $\langle c' v' \rangle = -\nu A_{ij} \partial \langle c \rangle / \partial x_j$ (12), results in a description of $\sigma^2$ that is in complete agreement with the pure advection reduction ($\alpha_{ij} = 0, \chi = 0$) of the model (16)–(17). This can be verified by taking derivatives of $\sigma^2$ (18) in space and time and substituting them into (17) and obtaining an equality. If the term $\langle c'^2 v' \rangle = -\nu A_{ij} \partial \sigma^2 / \partial x_j$ were dropped from the formulation, the important equivalence between (18) and our model, (16)–(17), under pure advection, is not obtained.

An unbounded growth of the CV with time is implied by (18):

$$CV = \left( \frac{c_0}{\langle c \rangle} - 1 \right)^{1/2} \quad t \to \infty \quad \langle c \rangle \to 0 \quad CV \to \infty. \quad (19)$$

The feature of an unboundedly growing concentration CV predicted in (19) is qualitatively different from what was observed in our numerical simulations (Figures 7 and 8). Data from large-scale subsurface tracer tests also do not exhibit the pure advection feature of an ever-increasing CV. In Figure 17 [from Kapoor and Gelhar, 1994b] is shown the estimated concentration CV from the bromide tracer test at Cape Cod. From the concentration data, the concentration values in a window around the center of mass were collected, and the CV estimated. The window size is proportional to the correlation length of the hydraulic conductivity. The empirical CV is shown to decrease slowly with time, as is observed in the

Figure 11b. Concentration microscales showing saturation at large time. Solid line, $t = 33.5 t_d$; long-dash line, $t = 36 t_d$; short-dash line, $t = 38.5 t_d$; $t_d = \left[2\nu \alpha_L (\lambda_1)^{-2} + 2\nu \alpha_T (\lambda_2)^{-2}\right]^{-1}$; $l_1 = 50$ cm, $l_2 = 10$ cm.

Figure 12a. Underestimation of peak concentration by the mean: variation with radius.

Figure 12b. Same as Figure 12a but for variation with time.

Figure 13. Volume occupied by solute: ratio of actual and apparent ($E/E_{\text{max}}$). Here $t_d = \left[2\nu \alpha_L (\lambda_1)^{-2} + 2\nu \alpha_T (\lambda_2)^{-2}\right]^{-1}$; VRT, variance residence time.
numerical simulations. The demise of the CV can be explained based on the simplified model (16)–(17), due to the effect of local dispersion ($\chi > 0$). Therefore, to predict the behavior of the CV using a Lagrangian approach will require correctly describing the effects of the interaction of heterogeneous advection and local dispersion on the concentration field. A failure to even crudely quantify these effects can lead to a qualitatively incorrect prediction that the CV does not decrease with time in a stationary flow field.

4.4. Time Integral Solution

Assuming $\langle c \rangle$ to initially be a finite-sized Gaussian, the solutions to (16) and (17) can be obtained using the classical Green’s function methodology applied to a linear advection diffusion equation with spatially constant parameters or, equivalently, by using the Fourier transform to convert (16) and (17) to initial value problems. For a diagonal effective dispersion tensor the solutions are

$$\langle c \rangle(x, t) = c_p(0) \prod_{i=1}^{N} \frac{\exp \left\{ -[x_i - X_i(t)]^2 / 2 R_i^2(t) \right\}}{R_i(t)/R_i(0)}$$

$$X_i(t) = X_i(0) + \delta_{i,vt} \quad R_i^2(t) = R_i^2(0) + 2 \int_{0}^{t} [A_{ii}(\tau) + \alpha_{ii}] d\tau$$

$$\sigma_i^2(x, t) = \sum_{i=1}^{N} \int_{0}^{t} F_i(x, t, \tau) d\tau$$

$$F_i(x, t, \tau) = 2 \nu A_{ii}(\tau) \exp \left\{ -\int_{\tau}^{t} \chi(\dot{\tau}) d\dot{\tau} \right\}$$

$$\left( 2 \nu \int_{0}^{t} [A_{ii}(\tau) + \alpha_{ii}] d\tau \right) \cdot \left( \frac{2 \nu \int_{0}^{t} [A_{ii}(\tau) + \alpha_{ii}] d\tau}{g_i(t, \tau) R_i^2(\tau)} + \frac{[x_i - X_i(t)]^2}{g_i(t, \tau)} \right)$$

$$\frac{\sigma_i}{\bar{c}}$$

$$\frac{VRT}{t_d}$$

Figure 14. Macrodispersivity for the mean and variance of concentration.

Figure 15. Evolution of the variance residence time (VRT); $t_d = \left[ 2 \nu \alpha_L(\lambda_1)^{-2} + 2 \nu \alpha_T(\lambda_2)^{-2} \right]^{-1}$.

Figure 16. Asymptotic variance residence time (VRT): variation with transverse local dispersivity. Here $t_d = \left[ 2 \nu \alpha_L(\lambda_1)^{-2} + 2 \nu \alpha_T(\lambda_2)^{-2} \right]^{-1}$.

Figure 17. Concentration CV for the Cape Cod bromide tracer. Here $w_i$, dimension of estimating window, located at the plume center; $\lambda_i$, correlation scale of hydraulic conductivity ($\lambda_1 = \lambda_2 = 260$ cm, $\lambda_3 = 19$ cm); $v$, mean velocity (42 cm/d); and $\alpha_{ij}$, local dispersivity ($\alpha_{11} = 0.5$ cm, $\alpha_{22} = \alpha_{33} = 0.05$ cm).
\[ \cdot c_j(0) \prod_{j=1}^{N} \exp \left\{ -[x_j - X_j(t)]^2 / g_j(t, \tau) \right\} \]

\[ g_j(t, \tau) = R_j^2(\tau) + 4v \int_0^\tau [A_j(\tau) + \alpha_j] \, d\tau \]

The time integral solution is evaluated by employing the numerically determined time-varying closure coefficients \( A_{11} \) (Figure 14) and VRT = \( \chi^{-1} \) (Figure 15). The radius of gyration of the plume \( R_1 \), predicted by the closure model, is compared with the results of the numerical simulations in Figure 5. The difference shows that there are some dispersive effects that are not contained in a Fickian flux model (12). At early time (Figure 4a) the concentration field clearly shows asymmetry due to the solute channeling into high conductivity zones. This asymmetry is not contained in the solution (20). However, \( \langle c \rangle \) is fairly well described at large time (Figure 6). For the hypothetical case of pure advection (\( \alpha_j = 0; \chi = 0 \)) it follows from (21) that the concentration CV increases with time; at the center of mass it was found to increase as \( t^{N/2} \), which is also implied by the classic pure advection result (18)–(19).

4.5. Large Time (\( t > \text{VRT}, R_i(t)/R_i(0) > 1 \)) Analytical Solution

Including the effects of local dispersion, the time integral solution (21) localizes at large times to yield simple expressions for \( \sigma_i^2 \). In the expressions below, \( A_{ij} \) and \( \chi = \text{VRT}^{-1} \) refer to their asymptotic value:

\[ \sigma_i^2 = \sum_{j=1}^{N} \left[ \frac{A_{ij}}{A_{ii} + \alpha_i} \left( \frac{\text{VRT}}{t} \right)^2 \langle c \rangle^2 + 2\nu A_{ii} \text{ VRT} \left( \frac{\partial \langle c \rangle}{\partial x_i} \right)^2 \right]. \]  

(22)

Away from the center of mass, the second term on the right-hand side of (22) can be shown to be dominant, which results in \( \sigma_i^2 \) being linearly related to the squared gradient of the mean concentration field:

\[ |x_i - v\delta_i|d > [\text{VRT}(A_{ii} + \alpha_i)v]^{1/2} \]

\[ \sigma_i^2 = \sum_{j=1}^{N} \left[ 2\nu A_{ii} \text{ VRT} \left( \frac{\partial \langle c \rangle}{\partial x_i} \right)^2 \right]. \]  

(23)

4.5.1. Production-dissipation balance. Equation (23) is the manifestation of a production-dissipation balance. The dominant balance in (17), away from the center of mass, is between the forcings on the right-hand side (as shown in Figure 10). In the original variance budget (7) this balance is expressed as

\[ -2\langle c'c\rangle \frac{\partial \langle c \rangle}{\partial x_i} = 2d_i \left\langle \frac{\partial c'}{\partial x_i} \frac{\partial \langle c \rangle}{\partial x_i} \right\rangle. \]  

(24)

In (24) at which the rate at which the interaction between the macro-dispersive transport and the mean gradient produces concentration variance is balanced by the rate at which local dispersion destroys it. At the center of mass this balance cannot occur because the gradient of the mean concentration field is zero. Notwithstanding that, the concentration can be quite irregular at the center of mass; the CV rose to a relatively high value (Figure 7). Therefore the transport of \( \sigma_i^2 \) from neighboring points needs to be accounted for.

The production-dissipation balance and the Schwarz inequality [Rudin, 1976] and the Fickian closure for the macro-dispersive flux (12) yield an approximate lower bound on VRT. This is illustrated for the macroscopically one-dimensional case (\( N = 1 \)):

\[ 2\nu A_{11} \left( \frac{\partial \langle c \rangle}{\partial x_1} \right)^2 \text{ production-dissipation balance} \]

\[ \sigma_i^2 \text{ Schwarz inequality} \quad \langle c'c' \rangle^2 \]

\[ \frac{\nu A_{11}(\partial \langle c \rangle/\partial x_1)^2}{\text{VRT} \sigma_i^2} = \frac{\nu A_{11}}{\text{VRT} \sigma_i^2} \]

\[ \Rightarrow \text{VRT} \geq \frac{\nu A_{11}}{2\sigma_i^2} \quad \equiv \frac{\Lambda^{n \text{advection-dominated transport}}}{2}, \]  

(25)

where \( \Lambda^{n}\) is the Lagrangian \( x \) velocity integral timescale.

4.5.2. Mean \( \langle c \rangle \) and standard deviation \( \sigma_i \). Figure 6 shows how the closure model predictions of \( \langle c \rangle \) and \( \sigma_i \) compare with that numerically determined. The bimodality of \( \sigma_i \) reflects the source term in the variance equation (17), which is the squared gradient of a Gaussian, hence having maxima at the inflection points of the mean concentration field (which are at a distance \( R_1 \) from the center). The temporal localization of the integrand in (21), due to local dispersion \( (\chi > 0) \), sustains the bimodality of \( \sigma_i \) at large times. On setting \( \chi = 0 \), the pure advection behavior of \( \sigma_i^2 \) can be studied using the model (16)–(17), with \( D_{ij} = \nu A_{ii} \) having an asymptotic value \( \sigma_i^2 \Lambda^{n}. \) It follows from the integral solution (21) that under heterogeneous advection alone, \( \sigma_i \) will become unimodal at large time.

4.5.3. Rise and fall of CV = \( \sigma_i^2/\langle c \rangle \). The growth and fall of the coefficient of variation is predicted by the solution (21) (Figures 7 and 8). From (21), the large time solution for the CV is

\[ \frac{\sigma_i^2}{\langle c \rangle} = \left\{ \sum_{i=1}^{N} \left[ \frac{A_{ii}}{A_{ii} + \alpha_i} \left( \frac{\text{VRT}}{t} \right)^2 \right]^{2/1/2} + 2\nu A_{ii} \text{ VRT} \left( \frac{\partial \ln \langle c \rangle}{\partial x_i} \right)^2 \right\}^{1/2}. \]  

(27)

The concentration CV at the center of mass follows

\[ \frac{\sigma_i^2}{\langle c \rangle} \text{ center} = \left\{ \sum_{i=1}^{N} \left[ \frac{A_{ii}}{A_{ii} + \alpha_i} \left( \frac{\text{VRT}}{t} \right)^2 \right]^{2n} \right\}^{1/2} A_{ii}^{1/2} \sigma_i \]

\[ \text{VRT} \ t. \]  

(28)

This behavior of the decaying CV is shown by the numerical simulation (Figures 7 and 8). The overall decrease of the CV with time is predicted by (21) for any finite value of VRT.

The concentration plots (Figure 4) and the CV plots (Figure 8) show that the concentration distribution is highly variable away from the center. This is because the gradient of the logarithm of the mean concentration increases with distance away from the center of mass (27). The approximated \( \sigma_i^2 \) budget (17) predicts a spatially nonuniform convergence of concentrations to the ensemble mean. Within a distance of \( n R_i \) from the center of mass, the CV is less than \( \{N[(\text{VRT}/t)^2 + n^2\text{VRT}/t]\}^{1/2} \).
Table 3. Properties of Concentration Fluctuations

<table>
<thead>
<tr>
<th>Numerical Observations Advection-Dispersion ((N = 1))</th>
<th>Theoretical Predictions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(|\sigma_r^2|)</td>
<td>early time growth and large time decay as (t^{-3/2})</td>
</tr>
<tr>
<td>(\sigma_r/c)_{\text{center}})</td>
<td>early time growth and large time decay as (t^{-1})</td>
</tr>
<tr>
<td>(\sigma_c)</td>
<td>bimodal at large times</td>
</tr>
<tr>
<td>(E/E_{\text{max}})</td>
<td>early time decrease and large time recovery to 1</td>
</tr>
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</table>

4.5.4. Global variance. The result from (21) and the numerical simulation, shown in Figure 9a, follow each other quite closely, in both growth and decay. This was expected because the rate of destruction of the global variance was used to numerically determine the VRT, which was employed in the solution (21), along with the numerically inferred \(A_{11}\). It follows from (21) that at large times,

\[
\|\sigma_r^2\| \propto t^{-1.5+N/2}. \quad (29)
\]

For the simulation, \(N = 1\); therefore the predicted decay is as \(t^{-3/2}\) (Figure 9). For the pure advection case, \(\|\sigma_r^2\|\) grows continually and approaches a constant value at large time, as is implied by (18).

4.5.5. Volume occupied by solute. Substituting a perturbation expansion of \(\ln c\) around \(\langle c \rangle\) in the expression for \(E(11)\), dropping terms involving triple perturbation products and higher, and using the Gaussianity of \(\langle c \rangle\) yields the estimate

\[
E/E_{\text{max}} = \exp \left\{ -\frac{1}{2} \frac{A_{11}}{\alpha_1} \left[ \frac{\text{VRT}}{t} + \left( \frac{\text{VRT}}{t} \right)^2 \right] \right\} \quad (30)
\]

Without local dispersion, this measure would asymptotically go toward zero as \(t^{-1/2}\).

5. Summary

The concentration of solute undergoing heterogeneous advection and local dispersion in a saturated random porous media, subjected to a hydraulic gradient, was examined in this work. For an impulse introduction of solute, the concentration variance budget can be approximated to derive simple expressions for the spatial-temporal evolution of concentration variance, employing two parameters, i.e., the variance residence time VRT and the effective dispersion coefficient \([\text{Kapoor and Gelhar, 1994a, b}]\), which can vary with time. The VRT is the characteristic time over which local dispersion destroys concentration fluctuations. The effective dispersion coefficient quantifies the rate of spreading of plumes. The resulting analytical description of concentration variance is in agreement with that found from detailed numerical simulations, when the overall spatial extent of the solute body is larger than the correlation scales of the hydraulic conductivity. Here is a summary of the description of concentration fluctuations (Table 3).

1. Owing to the action of local dispersion, the concentration coefficient of variation (CV) goes to zero at large time \((t > \text{VRT})\), albeit slowly and in a nonuniform manner. For example, at the center, \(CV = N^{1/2} \text{VRT}/t\). \(N\) denotes the number of spatial dimensions. This decrease is slow (not exponentially fast), and the VRT increases as local dispersion is reduced. At any given time, the CV increases unboundedly away from the center of mass. Therefore, despite the smoothing action of local dispersion, the fringes of plumes are highly irregular.

2. Away from the center of mass, at large time, the dominant balance in the concentration variance budget is between its rate of production and the rate of destruction due to local dispersion. This causes the concentration variance to be proportional to the squared gradient of the mean concentration field. Hence the variance has maxima at the points of maximum absolute values of the gradient of the mean concentration field. The production-dissipation balance and the Schwarz inequality yield a lower bound on the variance residence time, which is independent of the value of local dispersion coefficients when they are small.

3. At the center of mass a production dissipation balance is not possible. The transport of concentration fluctuations by local dispersion and, more important, due to heterogeneous advection need to be considered to quantify the concentration fluctuations at the center of mass.

4. The volume occupied by solute can be much smaller than what is apparent from its macroscopic dimensions, at early time. However, owing to local dispersion, at large time \((t \gg \text{VRT})\), in a stationary random media with finite scales of heterogeneity, the volume occupied by solute can be quantified by its macroscopic dimensions.

5. For the pure advection case the description of concentration variance made here is in complete agreement with the classic pure advection result. The inclusion of the potentially dominant transport mechanism of concentration variance \(\langle c^2 \nu'\rangle\) is necessary to obtain this agreement. Although the concentration standard deviation goes to zero at large time for both the pure advection case and on including local dispersion, without the action of local dispersion, it decreases slower than the mean concentration \(\langle c \rangle\). For the pure advection case the CV increases unboundedly with time, at the center \(CV \sim t^{N/4}\).

Connections between the porous media heterogeneity, local dispersion coefficients, and concentration macroscales need to be further explored to develop methods to predict the characteristic variance residence time (VRT), which was demonstrated in this work to control the evolution of concentration fluctuations and dilution.

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