ANALYSIS OF CONCENTRATION UNDER NON-ERGODIC TRANSPORT AS SAMPLED IN NATURAL AQUIFERS

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Abstract

The present paper considers the transport of a non-reactive solute in porous heterogeneous formations under non-ergodic conditions, i.e. when the injection volume is not larger than the characteristic size of the heterogeneity. A Lagrangian framework is developed in order to analyze the statistical properties of concentration fields as sampled in observation wells, with small diameter if compared to heterogeneity correlation scale. The methodology relies on a reverse formulation in which, instead of considering the forward tracking of the initial plume particles, the origin of the sampled particle is sought. Previous research showed that in the case of small values of the log-conductivity variance, σ_Y^2, analytical formulations for the mean, variance and pdf concentration are possible, while for high values of σ_Y^2 the concentration pdf, under ergodic conditions, can be fitted by a Beta function. In this work, a numerical procedure based on Monte Carlo analyses has been developed: the analyses show that, under non-ergodic transport, the uncertainty in the prediction of the barycenter of the plume may be described by a multi-normal random variate; this allows an estimate of the overall concentration pdf, which may be obtained by the convolution between the two distributions.

1. INTRODUCTION

Groundwater is probably the major source of water supply in the world, and the predictive ability in describing the fate of chemical contaminants in soils is of great importance when performing risk assessment and designing effective and efficient techniques to mitigate such problems.

Most of environmental regulations (e.g., U.S. EPA, 1988; European Union, Directive 80/778/EEC) define water quality standards and acceptability in terms of concentration thresholds, thus the prediction in natural aquifers should be performed with reference to the concentration probability of excess relative to the relevant threshold value.

Natural porous formations are inherently heterogeneous, and solute plumes transported exhibit irregular shapes. Transport of an inert solute in heterogeneous porous formations is determined by large-scale advection and pore-scale dispersion, the relative importance given by the Péclet number. The first is mainly controlled by the spatial variability of hydraulic conductivity, while the second, acting at scales lower than the heterogeneity characteristic length, is usually neglected.

The prediction of the concentration field, due to the irregular variation of permeability, is affected by uncertainty, which was set in a theoretical framework by regarding the permeability as a random space function. Several investigations were conducted, for small values of the log-conductivity variance, in order to define the first and second moment of concentration, both in Eulerian [Kapoor and Gelhar, 1994, Kapoor and Kitanidis, 1997, 1998] and in Lagrangian framework [Rubin et al., 1994, Bellin et al., 1994], for $Pe \to \infty$; [Dagan and Fiori, 1997, Fiori and Dagan, 1999, 2000], for finite Péclet values.

These studies were mainly focused on spatial moments analysis, some of them giving only an estimate of mean concentration and variance. [Fiorotto and Caroni, 2002], and [Caroni and Fiorotto, 2005] were the first to analyze the statistical properties of solute concentration in natural aquifers as sampled in observation wells, providing also expressions for the underlying pdf.

The aforementioned analyses were carried out under the ergodic hypothesis (satisfied when the solute initial characteristic lengths are much larger than the heterogeneity correlation scale), in which case the position of the barycenter of the plume can be regarded as deterministic. The ergodicity aspect was investigated quite recently [Dagan, 1990, 1991, Zhang et al., 1996, Caroni and Fiorotto, 2000, Zhang, 1998, 2003, Zhang and Seo, 2004, Fiori, 1998].

The aim of the present paper is to extend the research of [Fiorotto and Caroni, 2002] and [Caroni and Fiorotto, 2005], in particular analyzing under non-ergodic conditions the statistical properties of solute concentration as sampled in observation wells.

2. MATHEMATICAL FORMULATION

2.1. **Ergodic transport.** Consider a plume of elementary particles with volume V_0 at time $t = t_0$, whose dimensions are much larger than the heterogeneity correlation scale, λ; its transport is governed by two main mechanisms: (1) an advection displacement, $\mathbf{X}(t; \mathbf{a}, t_0, Pe)$, characterized by a correlation scale λ ($\mathbf{a}$ is the initial location of a particle and Pe represents the Péclet number); (2) a pore scale displacement, $\mathbf{X}_d(t)$, with characteristic length λ_d of the same order of magnitude of soil grains. The total particle trajectory can be written as [Dagan and Fiori, 1997]:

$$X_{T,j}(t; \mathbf{a}, t_0) = X_j(t; \mathbf{a}, t_0, Pe) + X_{d,j}(t) = \int_{t_0}^{t} v_j(\mathbf{X}_T(\tau; \mathbf{a}, t_0))\, d\tau + X_{d,j}(t) \qquad (1)$$

in which v_j is the random Eulerian velocity at the Darcy scale, and $\mathbf{X}_d(t)$ is modeled as a Brownian motion of zero mean and variance $X_{d,ij} = 2D_{d,ij}(t - t_0)$, $D_{d,ij}$ being the pore scale dispersion tensor.

The Péclet number $Pe = U\lambda/D_{d,11}$ (with U the mean flow velocity and $D_{d,11}$ the pore scale dispersion coefficient in the same direction as U) quantifies the relative weight of the two mechanisms: neglecting the pore scale effects leads to $Pe \to \infty$.

The displacements $\mathbf{X}$ and $\mathbf{X}_d$ are assumed as statistically independent in a first order approximation, since they are associated to two physically different processes with scale ratio λ/λ_d of the order of 10^3. This leads to the following result for the joint pdf:

$$f(\mathbf{X}, \mathbf{X}_d) = f_1(\mathbf{X}, t; \mathbf{a}, t_0, Pe)\, \phi(\mathbf{X}_d) \qquad (2)$$

in which ϕ is the normal pdf of the particle Brownian motion. Given an initial uniform concentration C_0, the concentration mean and mean square at a point $(\mathbf{x}, t)$ are respectively expressed as [Dagan and Fiori, 1997]:

$$\langle C(\mathbf{x},t)\rangle = C_0 \int d\mathbf{X} \int_{V_0} \phi(\mathbf{x}-\mathbf{X}) f_1(\mathbf{X},t;\mathbf{a},t_0,Pe)\, d\mathbf{a} \tag{3}$$

$$\langle C^2(\mathbf{x},t)\rangle = C_0^2 \int\int d\mathbf{X}^{(1)}\, d\mathbf{X}^{(2)} \tag{4}$$

$$\times \int_{V_0}\int_{V_0} \phi(\mathbf{x}-\mathbf{X}^{(1)})\phi(\mathbf{x}-\mathbf{X}^{(2)}) f_2(\mathbf{X}^{(1)},\mathbf{X}^{(2)},t;\mathbf{a}^{(1)},\mathbf{a}^{(2)},t_0,Pe)\, d\mathbf{a}^{(1)}\, d\mathbf{a}^{(2)}$$

where $f_1(\mathbf{X},t;\mathbf{a},t_0,Pe)$ and $f_2(\mathbf{X}^{(1)},\mathbf{X}^{(2)},t;\mathbf{a}^{(1)},\mathbf{a}^{(2)},t_0,Pe)$ are, respectively, the pdf of particle displacement $\mathbf{X}$ and the joint pdf of displacements $\mathbf{X}^{(1)}$ and $\mathbf{X}^{(2)}$ of two particles being at $t = t_0$ in positions $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(2)}$.

2.2. **Non-ergodic transport.** When the plume initial dimensions are of the same order of magnitude as λ, the trajectory of its barycenter is no more deterministic, and has to be considered as a random variable as follows:

$$\mathbf{X}_b = <\mathbf{X}_b> + \mathbf{X}'_b \tag{5}$$

The total displacement of an elementary particle can be expressed as [Fiori, 1998]:

$$\mathbf{X}_T = \mathbf{X} + \mathbf{X}_d = <\mathbf{X}> + \mathbf{X}' + \mathbf{X}_d = \mathbf{a} + \mathbf{U}\,t + \mathbf{X}' + \mathbf{X}_d \tag{6}$$

in which $\mathbf{X}'$ represents the fluctuation around the mean flow advection caused by $\mathbf{U}$, here assumed as $\mathbf{U} = (U, 0, 0)$. According to Figure 1, the barycenter of a non-ergodic plume is moving with a mean component $<\mathbf{X}_b> = \mathbf{A} + \mathbf{U}\,t$, where $\mathbf{A}$ represents its initial location; Eq. (6) may then be rewritten as:

$$\mathbf{X}_T = \mathbf{X}'_b + \mathbf{X}'' + \mathbf{X}_d = \mathbf{a} - \mathbf{A} + \mathbf{X}_b + (\mathbf{X}'' - \mathbf{a} - \mathbf{U}\,t) + \mathbf{X}_d \tag{7}$$

where $\mathbf{X}'' = \mathbf{X} - \mathbf{X}'_b$ represents the displacement of the particle due to the heterogeneity only.

Under such circumstances, and assuming the independency of the two processes, the total displacement pdf of one particle due to heterogeneity, $f_1(\mathbf{X},t;\mathbf{a},t_0,Pe)$, becomes:

$$f_1(\mathbf{X},t;\mathbf{a},t_0,Pe) = f_1(\mathbf{X}'',t;\mathbf{a},t_0,Pe)\,\phi_b(\mathbf{X}'_b) \tag{8}$$

in which f_1 now represents the pdf of displacement $\mathbf{X}''$ and ϕ_b is the pdf of the barycenter fluctuation $\mathbf{X}'_b$ (in the following sections it will be shown to be characterized by a gaussian distribution). By the same token, function f_2 becomes:

$$f_2(\mathbf{X}^{(1)},\mathbf{X}^{(2)},t;\mathbf{a}^{(1)},\mathbf{a}^{(2)},t_0,Pe) = f_2(\mathbf{X}''^{(1)},\mathbf{X}''^{(2)},t;\mathbf{a}^{(1)},\mathbf{a}^{(2)},t_0,Pe)\phi_b(\mathbf{X}'_b) \tag{9}$$

Taking into account also pore scale dispersion, Eqs. (2) and (8) lead to:

$$f(\mathbf{X},\mathbf{X}_d) = f_1(\mathbf{X}'',t;\mathbf{a},t_0,Pe)\,\phi_b(\mathbf{X}'_b)\,\phi(\mathbf{X}_d) \tag{10}$$

Finally, Eqs. (3) and (4) become respectively:

$$\langle C(\mathbf{x},t)\rangle = C_0 \int d\mathbf{X} \int d\mathbf{X}'' \int_{V_0} \phi(\mathbf{x}-\mathbf{X})\phi_b(\mathbf{X}-\mathbf{X}'') f_1(\mathbf{X}'',t;\mathbf{a},t_0,Pe)\, d\mathbf{a} \tag{11}$$

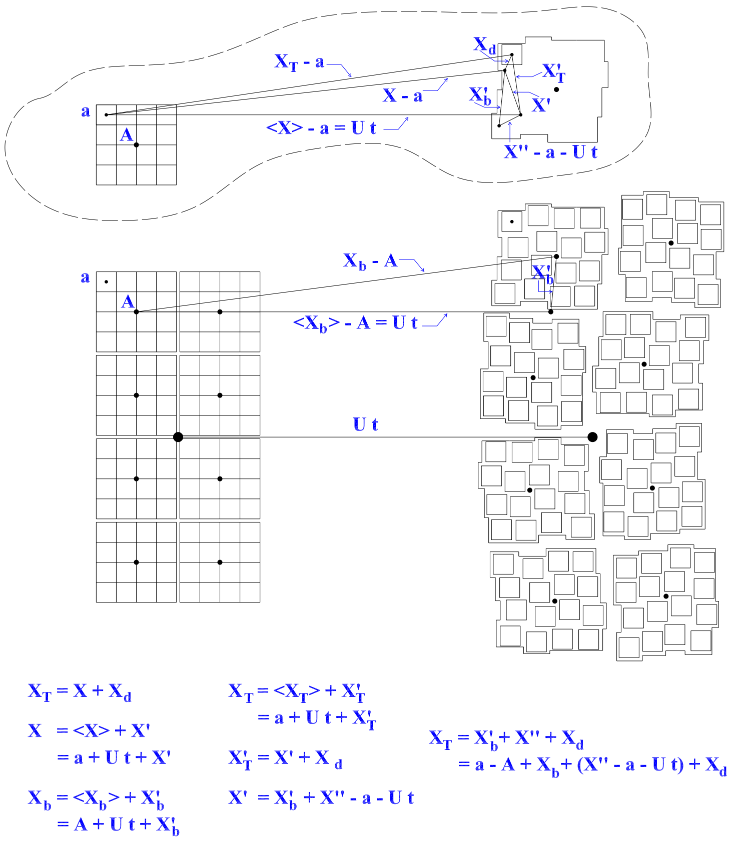

FIGURE 1. Subdivision of an ergodic plume in non-ergodic sub-plumes.

and

$$\langle C^2(\mathbf{x},t)\rangle = C_0^2 \int\int\int d\mathbf{X}''^{(1)}\, d\mathbf{X}''^{(2)}\, d\mathbf{X}'_b \int_{V_0}\int_{V_0} \phi(\mathbf{x}-\mathbf{X}''^{(1)})\phi(\mathbf{x}-\mathbf{X}''^{(2)}) \times f_2(\mathbf{X}''^{(1)},\mathbf{X}''^{(2)},t;\mathbf{a}^{(1)},\mathbf{a}^{(2)},t_0,Pe)\,\phi_b(\mathbf{X}'_b)\,d\mathbf{a}^{(1)}\,d\mathbf{a}^{(2)} \quad (12)$$

2.3. **Reverse formulation.** Equations (11) and (12) characterize concentration in the position $\mathbf{x}$ at time t, for instance as derived from field well samplings. The reverse formulation here adopted allows an easier solution of such equations: instead of moving forward from the injection volume V_0, it computes the initial location of the particle that, at time t, is in position $\mathbf{x}$ within the sampling volume. This allows considerable simplifications in calculus and in numerical simulations, especially when $V \ll V_0$.

According to the reverse scheme (for the details see [Fiorotto and Caroni, 2002] and [Caroni and Fiorotto, 2005]), equations (11) and (12) may be rewritten as:

$$\langle C(\mathbf{x},t)\rangle = C_0 \int d\mathbf{X} \int d\mathbf{X}'' \int_{V_0} \phi(\mathbf{a}-\mathbf{X})\phi_b(\mathbf{X}-\mathbf{X}'')f_1(\mathbf{X}'',t_0;\mathbf{x},t,Pe)\,d\mathbf{a} \quad (13)$$

and

$$\langle C^2(\mathbf{x},t)\rangle = C_0^2 \int\int\int d\mathbf{X}''^{(1)}\, d\mathbf{X}''^{(2)}\, d\mathbf{X}'_b \int_{V_0}\int_{V_0} \phi(\mathbf{a}^{(1)} - \mathbf{X}''^{(1)})\phi(\mathbf{a}^{(2)} - \mathbf{X}''^{(2)}) \times f_2(\mathbf{X}''^{(1)}, \mathbf{X}''^{(2)}, t_0; \mathbf{x}, t, Pe)\, \phi_b(\mathbf{X}'_b)\, d\mathbf{a}^{(1)}\, d\mathbf{a}^{(2)} \quad (14)$$

Extending the procedure given by [Caroni and Fiorotto, 2005], the pdf of concentration as sampled in volume V can be obtained. In particular, we consider the volume V as a single particle at the Darcy scale, and as a collection of N_p particles at the pore scale. At the Darcy scale, the displacement $\mathbf{X} = \mathbf{X}'' + \mathbf{X}'_b$ is distributed according to Eq. (8) which, according to the reverse scheme, becomes:

$$f_1(\mathbf{a}, t; \mathbf{X}, t_0, Pe) = f_1(\mathbf{X}'', t; \mathbf{X}, t_0, Pe)\, \phi_b(\mathbf{X}'_b) \quad (15)$$

Since the total displacement of one particle is $\mathbf{X}_T = \mathbf{X} + \mathbf{X}_d$, the probability that a single particle falls within V_0 having started its motion in V, conditional on $\mathbf{X}$ and according to the reverse formulation, is:

$$p_{\mathbf{x}} = \int_{V_0} \phi(\xi + \mathbf{X} - \mathbf{x})\, d\xi \quad (16)$$

in which ξ has origin in the center of mass of V_0 placed at a distance $\mathbf{x}$ from V. If n out of the N_p particles fall in V_0, the concentration in V can be calculated as [Caroni and Fiorotto, 2005]:

$$C = C_0 \frac{n}{N_p} \quad (17)$$

Thus, the probability of C can be evaluated as the probability of n successes out of N_p independent trials, and its distribution is binomial:

$$\text{prob}\left(C = C_0 \frac{n}{N_p}\right) = \binom{N_p}{n} \int d\mathbf{X}'' \int f_1(\mathbf{X}'')\phi_b(\mathbf{X} - \mathbf{X}'') p_{\mathbf{x}}^n (1 - p_{\mathbf{x}})^{N_p - n}\, d\mathbf{X} \quad (18)$$

where $\binom{N_p}{n}$ is the binomial coefficient.

3. RESULTS AND DISCUSSION

The numerical procedure adopted is based on Monte Carlo analysis, and is described in detail in [Caroni and Fiorotto, 2005]. The methodology was applied to a 2D aquifer characterized by an extension of 64×64 heterogeneity integral scales and with different values of σ_y^2. Péclet number was varied in the range 10÷10,000, while several initial plume dimensions were investigated. The number of Monte Carlo simulations was between 1000 and 5000, depending on the plume size while, for each Monte Carlo, $N_p = 100$ particles at the pore scale level was adopted.

In the following, results related to thin plumes initially normal to the mean flow direction are given. In particular, their dimension along the mean flow was kept constant and equal to $\lambda/4$, while transversally it was varied between λ and 10λ. The cumulative distribution functions of concentration at several expected centroid positions with $\sigma_y^2 = 0.05$ are plotted in Figure 2 for $Pe = 1000$ and in Figure 3 for $Pe = 10$.

From the results obtained, the following observations can be done.

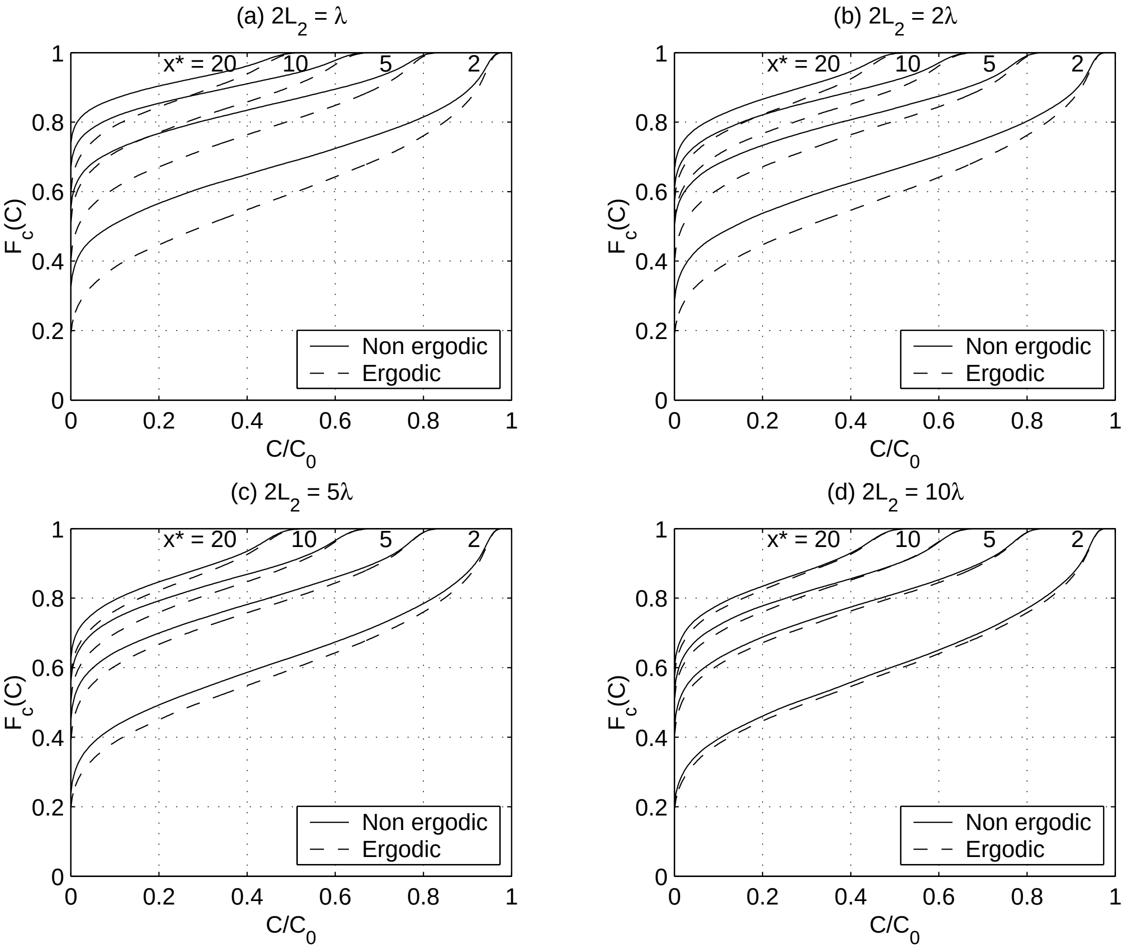

Figure 2. Cumulative distribution functions of concentration at expected centroid positions for $\sigma_y^2 = 0.05$ and $Pe = 1000$, under ergodic (dashed) and non-ergodic (solid line) conditions. Numbers refer to the location $x^* = x/\lambda = Ut/\lambda$. Initial plume size is in all cases $2L_1 = 0.25\lambda$ along the mean flow direction. Transverse plume size is (a) λ; (b), 2λ; (c), 5λ; (d), 10λ.

(1) Cumulative distribution functions under non-ergodic conditions are always higher than the values obtained for the ergodic case, irrespective of the initial plume size and log-conductivity variance value. In other words, keeping the same level of probability, concentration values for non ergodic conditions are lesser than the ergodic case. Although not shown in the figures, this is more evident as σ_y^2 increases, indicating a stronger spreading of the plume and larger uncertainty about its centroid in high heterogeneous media, in agreement with what found by [Zhang, 2004] for spatial moments and plume centroid variances.

(2) Concentration pdf approaches its ergodic limit as the initial plume size increases. Simulations carried out with other plume sizes showed that an initial large transverse length is more important than a longitudinal large source plume in reaching ergodic conditions.

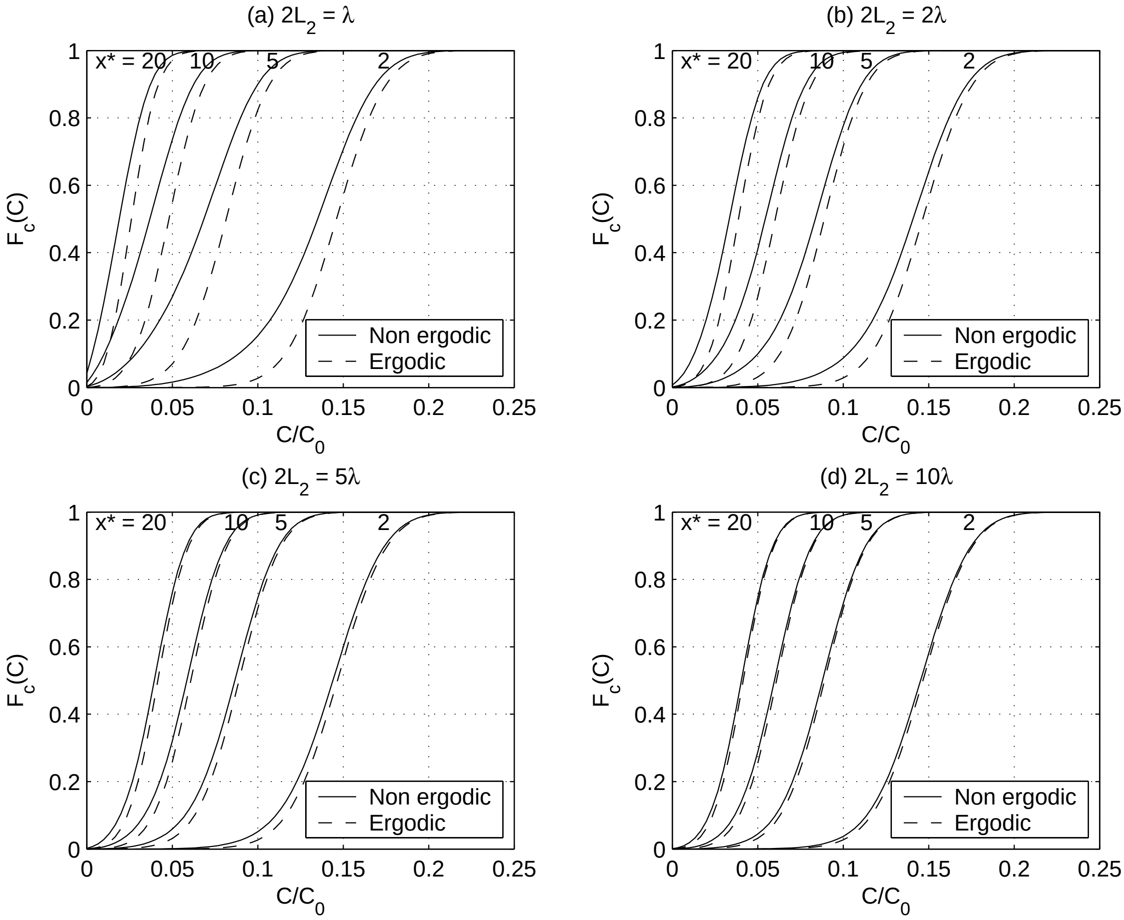

FIGURE 3. Cumulative distribution functions of concentration at expected centroid positions for $\sigma_y^2 = 0.05$ and $Pe = 10$, under ergodic (dashed) and non-ergodic (solid line) conditions. Numbers refer to the location $x^* = x/\lambda = Ut/\lambda$. Initial plume size is in all cases $2L_1 = 0.25\lambda$ along the mean flow direction. Transverse plume size is (a) λ; (b), 2λ; (c), 5λ; (d), 10λ.

(3) Péclet number plays an important role in the dispersion process: comparing Figures 2 and 3, there is a remarkable difference between distribution functions. In the case of $Pe = 1000$, Figure 2, a non-zero probability mass is present at $C/C_0 = 0$, ranging from 0.2 up to 0.8 depending on plume center position and initial size; in particular, these values decrease when decreasing travel time or increasing initial plume transverse dimension. For $Pe = 10$, Figure 3, such values for $C/C_0 = 0$ go to zero, indicating the effect caused by pore scale dispersion.

(4) The ergodic condition is fairly approximated in the case $2L_2 = 10\lambda$. This appears to happen earlier at lower Pe values, as can be observed when comparing the case $2L_2 = 5\lambda$ at $Pe = 1000$, Figure 2, and $Pe = 10$, Figure 3, due to spreading induced by pore scale effects, especially in the first stages of the dispersion process. Considering concentration as an averaging operator over particle positions, this result can be considered in agreement with results obtained at $Pe \to \infty$ [Zhang,

2003] who found that ergodicity in particle displacement moments may actually not be reached even for line sources as large as 20 integral scales normal to the mean flow, and by [Salandin and Fiorotto, 1993] who found that this condition is met for transverse sizes of at least 25 integral scales.

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