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Analysis of One-Dimensional Solute Transport Through Porous Media With Spatially Variable Retardation Factor

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A closed-form analytical small-perturbation (or first-order) solution to the one-dimensional advection-dispersion equation with spatially variable retardation factor is derived to investigate the transport of sorbing but otherwise nonreacting solutes in hydraulically homogeneous but geochemically heterogeneous porous formations. The solution is developed for a third- or flux-type inlet boundary condition, which is applicable when considering resident (volume-averaged) solute concentrations, and a semi-infinite porous medium. For mathematical simplicity it is hypothesized that the sorption processes are based on linear equilibrium isotherms and that the local chemical equilibrium assumption is valid. The results from several simulations, compared with predictions based on the classical advection-dispersion equation with constant coefficients, indicate that at early times, spatially variable retardation affects the transport behavior of sorbing solutes. The zeroth moments corresponding to constant and variable retardation are not necessarily equal. The impact of spatially variable retardation increases with increasing Péclet number. The center of mass appears to move more slowly, and solute spreading is enhanced in the variable retardation case. At late times, when the travel distance is much larger than the correlation scale of the retardation factor, the zeroth moment for the variable retardation case is identical to the case of invariant retardation. The small-perturbation solution agrees closely with a finite difference numerical approximation.

INTRODUCTION

The impact of spatially variable hydraulic parameters on the transport and spreading of conservative, nonreacting solutes in natural subsurface systems has been the focus of many recent studies. *Gelhar et al.* [1979], *Matheron and de Marsily* [1980], *Simmons* [1982], *Gelhar and Axness* [1983], *Dagan*, [1982, 1984, 1987], *Koch and Brady* [1987], *Neuman et al.* [1987], and *Kitanidis* [1988], among others, have provided methodologies for improving the description and prediction of nonreacting solute transport in complex-structured formations, compared with the prediction based on the classical advection-dispersion equation with constant coefficients. On the other hand, the transport of sorbing solutes in geochemically as well as hydraulically heterogeneous porous media has received little attention.

For the important case of transport of sorbing solutes in geochemically homogeneous porous media, the effects of sorption are commonly accounted for by a dimensionless retardation factor [*Hashimoto et al.*, 1964], which may be defined as the ratio of the average interstitial fluid velocity to the propagation velocity of the solute. Excluding the possibilities of mass transport limitations and solute transformation or decay, any observed fluctuations on the retardation factor are attributed solely to the variability of the distribution coefficient, which is an experimentally obtained measure of sorption or solute retention by the solid formation. Sorption processes can be complex and depend on many variables, including temperature, pressure, solution *p*H, and ionic strength, sorbent surface charge, sorbent sorptive capacity, and the presence of species that compete for sorption sites. Spatial or temporal fluctuations in any of these variables accordingly affect the distribution coefficient and, consequently, the movement of sorbing solutes in subsurface porous media. For example, the distribution coefficient of nonpolar organic solutes (synthetic organic chemicals, major constituents of groundwater toxic pollutants) is correlated with the organic carbon content of the sorbent [*Karickhoff*, 1984]. Although such a correlation is not fully reliable for every solute-sorbent system [*Curtis and Roberts*, 1985; *Curtis et al.*, 1986; *Mackay et al.*, 1986], it can explain to some extent the variable retardation observed in field experiments [*Roberts et al.*, 1986].

Garabedian [1987] employed spectral methods to analyze reactive solute macrodispersion under the assumption that the log-hydraulic conductivity is linearly related to both the porosity and the distribution coefficient. His results indicate that solute spreading is enhanced when there is negative correlation between the log-hydraulic conductivity and the distribution coefficient. Also, *van der Zee and van Riemsdijk* [1987] derived an expression for the field-averaged profile of sorbed solute concentration, assuming that spatially variable soil formations can be represented by a bundle of noninteracting parallel homogeneous columns which differ with respect to fluid velocity, retardation factor, and time period of solute input. These parameters are assumed lognormally distributed. Finally, *Valocchi* [1989] recently employed Taylor-Aris spatial moment analysis to study the long-time asymptotic behavior of kinetically sorbing solute transport in perfectly stratified porous media, assuming that pore water velocity, dispersion coefficients, distribution coefficient, and adsorption rate coefficient are vertically distributed. The results of this study confirm that negative correlation between the vertical profiles of pore water velocity and retardation factor may increase solute dispersion.

The present work is focused on the transport of sorbing but otherwise nonreacting solutes under local equilibrium conditions in a one-dimensional hydraulically homogeneous but geochemically heterogeneous porous medium. Analytical procedures are employed to solve the one-dimensional advection-dispersion equation with uniform, steady fluid flow conditions and spatially variable retardation factor, for a semi-infinite medium and flux-type inlet boundary condi-

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tion. Although an exponential autocovariance function is used in this study, the analytical expression derived here is sufficiently general that any other autocovariance function for the perturbed retardation factor can be readily employed. The impact of spatially variable sorption on solute transport in porous media is investigated. The analytical first-order solution is compared with a numerical approximation based on a finite difference scheme.

The results of this investigation are well suited for design and interpretation of experiments in laboratory-packed columns and possibly some field studies where the assumption of one-dimensional flow under constant velocity and constant dispersion coefficient is valid. Our experience with solute transport experiments in an induced flow field between an injection-extraction well pair suggests that in some cases one-dimensional transport models with constant coefficients are adequate for the field scale [*Chrysikopoulos et al.*, 1990]. The methodology of this work can provide a starting point for generalization to the solution of more complicated physical systems and multidimensional solute transport models.

TRANSPORT MODEL

The transport of a sorbing solute through a one-dimensional porous medium under steady state flow conditions is governed by the following partial differential equation [*Lapidus and Amundson*, 1952]:

$$\frac{\partial c(t, x)}{\partial t} + \frac{\rho}{\theta}\frac{\partial c^*(t, x)}{\partial t} = D\frac{\partial^2 c(t, x)}{\partial x^2} - U\frac{\partial c(t, x)}{\partial x} \tag{1}$$

where $c(t, x)$ is the volume-averaged or resident liquid-phase solute concentration, which is defined as the solute mass per unit volume of interstitial fluid, as opposed to the flux-averaged concentration which corresponds to the solute mass per unit volume of fluid flowing through a given cross section per unit time, $c^*(t, x)$ is the solid-phase concentration of the sorbed solute per unit mass of solids, D is the hydrodynamic dispersion coefficient, U is the average interstitial fluid velocity, x is the spatial coordinate in the direction of flow, t is time, ρ is the bulk density of the solid matrix, and θ is porosity. For linear, reversible, instantaneous sorption, the equilibrium relationship between the solute substance in the aqueous and solid phases is given by

$$c^*(t, x) = K_d(x)c(t, x) \tag{2}$$

where $K_d(x)$ is the partition or distribution coefficient. The distribution coefficient is expressed as the ratio of solute concentration on the adsorbent to solute aqueous concentration at equilibrium. Combining (1) and (2) leads to

$$R(x)\frac{\partial c(t, x)}{\partial t} = D\frac{\partial^2 c(t, x)}{\partial x^2} - U\frac{\partial c(t, x)}{\partial x} \tag{3}$$

The dimensionless variable $R(x)$ is the retardation factor, introduced by *Hashimoto et al.* [1964], defined as

$$R(x) = 1 + \frac{\rho}{\theta}K_d(x) \tag{4}$$

Traditionally, in solute transport mathematical modeling the retardation factor is considered constant throughout the porous medium. However, in the present analysis it is assumed that the retardation factor fluctuates along the spatial coordinate.

For a semi-infinite system, the appropriate initial and boundary conditions that lead to correct evaluation of resident concentrations are [*van Genuchten and Parker*, 1984]

$$c(0, x) = 0 \tag{5a}$$

$$\begin{aligned} -D\frac{\partial c(t, 0)}{\partial x} + Uc(t, 0) &= Uc_p \qquad 0 < t \le t_p \\ -D\frac{\partial c(t, 0)}{\partial x} + Uc(t, 0) &= 0 \qquad t > t_p \end{aligned} \tag{5b}$$

$$\frac{\partial c(t, \infty)}{\partial x} = 0 \tag{5c}$$

where c_p is the pulse-type injection concentration and t_p is the duration of the solute pulse. The condition (5*a*) corresponds to the situation in which the solute is initially absent from the one-dimensional porous medium. The third- or flux-type boundary condition (5*b*) for pulse injection implies concentration discontinuity at the inlet and leads to material balance conservation [*Brigham*, 1974; *Choi and Perlmutter*, 1976; *Kreft and Zuber*, 1978; *Parker and van Genuchten*, 1984]. The downstream boundary condition (5*c*) preserves concentration continuity for a semi-infinite system.

It is generally more convenient to work with models written in dimensionless variables. By employing the following definitions,

$$C = \frac{c}{c_p} \tag{6}$$

$$X = \frac{x}{l} \tag{7}$$

$$T = \frac{Ut}{l} \tag{8}$$

$$T_p = \frac{Ut_p}{l} \tag{9}$$

$$Pe = \frac{Ul}{D} \tag{10}$$

where l is the correlation scale of the retardation factor, the model equations (3) and (5) become

$$R(X)\frac{\partial C(T, X)}{\partial T} = \frac{1}{Pe}\frac{\partial^2 C(T, X)}{\partial X^2} - \frac{\partial C(T, X)}{\partial X} \tag{11}$$

$$C(0, X) = 0 \tag{12a}$$

$$\begin{aligned} -\frac{1}{Pe}\frac{\partial C(T, 0)}{\partial X} + C(T, 0) &= 1 \qquad 0 < T \le T_p \\ -\frac{1}{Pe}\frac{\partial C(T, 0)}{\partial X} + C(T, 0) &= 0 \qquad T > T_p \end{aligned} \tag{12b}$$

$$\frac{\partial C(T, \infty)}{\partial X} = 0 \tag{12c}$$

ANALYTICAL SMALL-PERTURBATION SOLUTION

The retardation factor and, consequently, the solute concentration are considered to be stochastic processes. The retardation factor is assumed stationary with mean $\langle R\rangle = E[R(X)]$, where the angle brackets signify ensemble mean or expected value. The concentration is both nonstationary and time dependent. In this work we solve for the concentration mean $\langle C\rangle(T, X) = E[C(T, X)]$. The retardation factor and the solute concentration are expressed as

$$R(X) = \langle R\rangle + R'(X) \tag{13a}$$

$$C(T, X) = \langle C\rangle(T, X) + C'(T, X) \tag{13b}$$

where the prime signifies fluctuations, and $E[C'(T, X)] = 0$ and $E[R'(X)] = 0$. Substituting (13) into (11) yields

$$[\langle R\rangle + R'(X)]\left(\frac{\partial\langle C\rangle(T, X)}{\partial T} + \frac{\partial C'(T, X)}{\partial T}\right) = \frac{1}{Pe}\left(\frac{\partial^2\langle C\rangle(T, X)}{\partial X^2} + \frac{\partial^2 C'(T, X)}{\partial X^2}\right) - \left(\frac{\partial\langle C\rangle(T, X)}{\partial X} + \frac{\partial C'(T, X)}{\partial X}\right) \tag{14}$$

The stochastic partial differential equation of interest is obtained by taking the ensemble averages of all terms in (14). This equation is

$$\langle R\rangle\frac{\partial\langle C\rangle(T, X)}{\partial T} + \left\langle R'(X)\frac{\partial C'(T, X)}{\partial T}\right\rangle = \frac{1}{Pe}\frac{\partial^2\langle C\rangle(T, X)}{\partial X^2} - \frac{\partial\langle C\rangle(T, X)}{\partial X} \tag{15}$$

Similarly, the ensemble-averaged initial and boundary conditions are attained by substituting (13*b*) into (12) and taking expected values

$$\langle C\rangle(0, X) = 0 \tag{16a}$$

$$-\frac{1}{Pe}\frac{\partial\langle C\rangle(T, 0)}{\partial X} + \langle C\rangle(T, 0) = 1 \qquad 0 < T \le T_p$$

$$-\frac{1}{Pe}\frac{\partial\langle C\rangle(T, 0)}{\partial X} + \langle C\rangle(T, 0) = 0 \qquad T > T_p \tag{16b}$$

$$\frac{\partial\langle C\rangle(T, \infty)}{\partial X} = 0 \tag{16c}$$

If the $\langle R'(X)\partial C'(T, X)/\partial T\rangle$ term were a given function of T and X, the general solution to (15) subject to initial/boundary conditions (16) could be obtained from the work of *Ito* [1957*a*, *b*], as summarized by *Sato and Ueno* [1965], and is given by

$$\langle C\rangle(T, X) = Q(T, X) \qquad 0 < T \le T_p$$

$$\langle C\rangle(T, X) = Q(T, X) - Q(T - T_p, X) \qquad T > T_p \tag{17a}$$

where

$$Q(T, X) = \int_0^T d\tau \int_0^\infty F(T - \tau, X, \lambda)\Phi(\tau, \lambda)\, d\lambda + \int_0^T F(T - \tau, X, 0)\Psi(\tau, 0)\, d\tau \tag{17b}$$

$$\Phi(T, X) = -\left\langle\frac{R'(X)}{\langle R\rangle}\frac{\partial C'(T, X)}{\partial T}\right\rangle \tag{17c}$$

$$\Psi(T, 0) = \frac{1}{\langle R\rangle} \tag{17d}$$

and $F(T, X, \xi)$ is known as the "fundamental solution" to the point-source homogeneous form of the equation [*Zauderer*, 1983] that satisfies the following partial differential equation and initial/boundary conditions

$$\langle R\rangle\frac{\partial F(T, X, \xi)}{\partial T} = \frac{1}{Pe}\frac{\partial^2 F(T, X, \xi)}{\partial X^2} - \frac{\partial F(T, X, \xi)}{\partial X} \tag{18a}$$

$$F(0, X, \xi) = \delta(X - \xi) \tag{18b}$$

$$-\frac{1}{Pe}\frac{\partial F(T, 0, \xi)}{\partial X} + F(T, 0, \xi) = 0 \tag{18c}$$

$$\frac{\partial F(T, \infty, \xi)}{\partial X} = 0 \tag{18d}$$

The function $F(T, X, \xi)$ is obtained by straightforward but laborious procedures. Taking the Laplace transforms with respect to time and space of (18*a*)–(18*d*), using the transformed boundary conditions and applying inverse transformations yields (see Appendix A)

$$F(T, X, \xi) = \left(\frac{Pe\,\langle R\rangle}{4\pi T}\right)^{1/2}\exp\left[\frac{Pe(X - \xi)}{2}\right]\cdot\exp\left[-\frac{Pe\,\langle R\rangle(X - \xi)^2}{4T} - \frac{Pe\,T}{4\langle R\rangle}\right] + \left(\frac{Pe\,\langle R\rangle}{4\pi T}\right)^{1/2}\exp\left[\frac{Pe(X - \xi)}{2}\right]\cdot\exp\left[-\frac{Pe\,\langle R\rangle(X + \xi)^2}{4T} - \frac{Pe\,T}{4\langle R\rangle}\right] - \left(\frac{Pe}{2}\right)\exp[Pe\,X]\,\mathrm{erfc}\left[\left(\frac{Pe\,T}{4\langle R\rangle}\right)^{1/2} + \left(\frac{Pe\,\langle R\rangle}{4T}\right)^{1/2}(X + \xi)\right] \tag{19}$$

Thus the problem reduces to how to evaluate the term $\langle R'(X)\partial C'(T, X)/\partial T\rangle$. This term accounts for the effects of spatial variability in the retardation factor. Readers familiar with the study of turbulence will recognize that this term plays a role similar to that of Reynolds stresses. The remaining part of this section is devoted to the derivation of this term.

The solution is derived by the method of small-perturbations or first-order approximation. This method is

described elsewhere [e.g., *Van Dyke*, 1975] and has been applied in numerous groundwater flow and solute transport studies [e.g., *Gelhar and Axness*, 1983; *Dagan*, 1985; *Hoeksema and Kitanidis*, 1984]. The method is as follows. The fluctuations are assumed to be small. To keep track of what are the small terms, a dimensionless scalar ε, is introduced. Thus the fluctuations are written

$$R'(X) = \varepsilon^1 R_1'(X)$$
$$C'(T, X) = \varepsilon^1 C_1'(T, X) + \cdots \tag{20}$$

and the mean values

$$\langle R\rangle = \varepsilon^0\langle R_0\rangle$$
$$\langle C\rangle(T, X) = \varepsilon^0\langle C_0\rangle(T, X) + \varepsilon^1\langle C_1\rangle(T, X) + \cdots \tag{21}$$

where the subscript zero indicates zero-order terms, the subscript 1 first-order terms, etc. Note that only a zero-order perturbation is performed for the mean retardation factor, because $R(X)$ is assumed stationary. The introduction of ε is solely a mathematical artifice which permits separation of the "small" high-order terms from the larger low-order terms, and bookkeeping of terms of the same order. Substituting (20) and (21) into the governing equation (14) leads to

$$\begin{aligned}&[\varepsilon^0\langle R_0\rangle + \varepsilon^1 R_1'(X)]\\ &\cdot\left(\varepsilon^0\frac{\partial\langle C_0\rangle(T, X)}{\partial T} + \varepsilon^1\frac{\partial\langle C_1\rangle(T, X)}{\partial T} + \varepsilon^1\frac{\partial C_1'(T, X)}{\partial t}\right)\\ &= \frac{1}{Pe}\left(\varepsilon^0\frac{\partial^2\langle C_0\rangle(T, X)}{\partial X^2} + \varepsilon^1\frac{\partial^2\langle C_1\rangle(T, X)}{\partial X^2} + \varepsilon^1\frac{\partial^2 C_1'(T, X)}{\partial X^2}\right)\\ &- \left(\varepsilon^0\frac{\partial\langle C_0\rangle(T, X)}{\partial X} + \varepsilon^1\frac{\partial\langle C_1\rangle(T, X)}{\partial X} + \varepsilon^1\frac{\partial C_1'(T, X)}{\partial X}\right)\end{aligned} \tag{22}$$

This is equation must be satisfied separately for terms of each order. Equating coefficients of ε^0 into (22) yields the familiar deterministic advection-dispersion equation with constant coefficients

$$\langle R_0\rangle\frac{\partial\langle C_0\rangle(T, X)}{\partial T} = \frac{1}{Pe}\frac{\partial^2\langle C_0\rangle(T, X)}{\partial X^2} - \frac{\partial\langle C_0\rangle(T, X)}{\partial X} \tag{23}$$

The solution to (23), subject to initial and boundary conditions (16*a*)–(16*c*), where $\langle C\rangle(T, X)$ is replaced by $\langle C_0\rangle(T, X)$, has been presented by *Lindstrom et al.* [1967] and *Gershon and Nir* [1969]:

$$\langle C_0\rangle(T, X) = A(T, X) \qquad 0 < T \le T_p$$
$$\langle C_0\rangle(T, X) = A(T, X) - A(T - T_p, X) \qquad T > T_p \tag{24a}$$

where

$$A(T, X) = \tfrac{1}{2}\operatorname{erfc}\left[\left(\frac{Pe}{4\langle R_0\rangle T}\right)^{1/2}(\langle R_0\rangle X - T)\right] + \left(\frac{Pe\,T}{\pi\langle R_0\rangle}\right)^{1/2}\exp\left[-\frac{Pe(\langle R_0\rangle X - T)^2}{4\langle R_0\rangle T}\right]$$
$$-\frac{1}{2}\left(1 + Pe\,X + \frac{Pe\,T}{\langle R_0\rangle}\right)\exp[Pe\,X]\cdot\operatorname{erfc}\left[\left(\frac{Pe}{4\langle R_0\rangle T}\right)^{1/2}(\langle R_0\rangle X + T)\right] \tag{24b}$$

Equating coefficients of ε^1 into (22) yields the stochastic parabolic partial differential equation

$$\langle R_0\rangle\frac{\partial\langle C_1\rangle(T, X)}{\partial T} + \langle R_0\rangle\frac{\partial C_1'(T, X)}{\partial T} + R_1'(X)\frac{\partial\langle C_0\rangle(T, X)}{\partial T} = \frac{1}{Pe}\frac{\partial^2\langle C_1\rangle(T, X)}{\partial X^2} + \frac{1}{Pe}\frac{\partial^2 C_1'(T, X)}{\partial X^2} - \frac{\partial\langle C_1\rangle(T, X)}{\partial X} - \frac{\partial C_1'(T, X)}{\partial X} \tag{25}$$

Taking expected values of all terms leads to

$$\langle R_0\rangle\frac{\partial\langle C_1\rangle(T, X)}{\partial T} = \frac{1}{Pe}\frac{\partial^2\langle C_1\rangle(T, X)}{\partial X^2} - \frac{\partial\langle C_1\rangle(T, X)}{\partial X} \tag{26}$$

This is a deterministic boundary value problem with homogeneous initial/boundary conditions obtained from (12) by keeping first-order terms and taking expected values. By inspection, we can deduce that the solution is $\langle C_1\rangle(T, X) = 0$.

Subtracting (26) from (25), we obtain the stochastic partial differential equation which relates the fluctuation $C_1'(T, X)$ to the fluctuation $R_1'(X)$

$$\langle R_0\rangle\frac{\partial C_1'(T, X)}{\partial T} + R_1'(X)\frac{\partial\langle C_0\rangle(T, X)}{\partial T} = \frac{1}{Pe}\frac{\partial^2 C_1'(T, X)}{\partial X^2} - \frac{\partial C_1'(T, X)}{\partial X} \tag{27}$$

subject to the following initial and boundary conditions

$$C_1'(0, X) = 0 \tag{28a}$$

$$-\frac{1}{Pe}\frac{\partial C_1'(T, 0)}{\partial X} + C_1'(T, 0) = 0 \tag{28b}$$

$$\frac{\partial C_1'(T, \infty)}{\partial X} = 0 \tag{28c}$$

If we consider $R_1'(X)$ given, the general solution to the boundary value problem is [*Sato and Ueno*, 1965]

$$C_1'(T, X) = \int_0^T d\tau\int_0^\infty F(T - \tau, X, \lambda)h(\tau, \lambda)\,d\lambda \tag{29}$$

where $F(T, X, \lambda)$ is defined in (19), $h(T, X)$ is given by

$$h(T, X) = -\frac{R_1'(X)}{\langle R_0\rangle}\frac{\partial\langle C_0\rangle(T, X)}{\partial T} = -\frac{R_1'(X)}{\langle R_0\rangle}\Omega(T, X) \tag{30}$$

and the term $\Omega(T, X) = \partial\langle C_0\rangle(T, X)/\partial T$ in (30) is obtained by differentiating (24) with respect to dimensionless time

$$\Omega(T, X) = \frac{\partial \langle C_0 \rangle(T, X)}{\partial T} = A_T(T, X) \qquad 0 < T \leq T_p \tag{31a}$$

$$\Omega(T, X) = \frac{\partial \langle C_0 \rangle(T, X)}{\partial T} = A_T(T, X) - A_T(T - T_p, X) \qquad T > T_p$$

where

$$A_T(T, X) = \left(\frac{Pe}{\pi \langle R_0 \rangle T}\right)^{1/2} \exp\left[-\frac{Pe(\langle R_0 \rangle X - T)^2}{4\langle R_0 \rangle T}\right] - \left(\frac{Pe}{2\langle R_0 \rangle}\right) \exp[Pe\, X]\, \text{erfc}\left[\left(\frac{Pe}{4\langle R_0 \rangle T}\right)^{1/2} (\langle R_0 \rangle X + T)\right] \tag{31b}$$

Employing (20), (29), and (30), the expression for the second term on the left-hand side of (15) can be approximated by the second-order term:

$$\left\langle R'(X) \frac{\partial C'(T, X)}{\partial T} \right\rangle \simeq E\left[\varepsilon^{-1} R_1'(X) \frac{\varepsilon^{-1} C_1'(T, X)}{\partial T}\right] = \varepsilon^2 E\left[R_1'(X) \frac{\partial}{\partial T} \int_0^T d\tau \int_0^\infty F(T - \tau, X, \lambda) h(\tau, \lambda)\, d\lambda\right] = -\frac{\varepsilon^2}{\langle R_0 \rangle} \int_0^T d\tau \int_0^\infty \cdot \frac{\partial F(T - \tau, X, \lambda)}{\partial T} E[R_1'(X) R_1'(\lambda)] \Omega(\tau, \lambda)\, d\lambda \tag{32}$$

where expectation was interchanged with integration and, subsequently, Leibniz's theorem for differentiation of an integral was employed [*Abramowitz and Stegun*, 1972]. The term $\partial F(T - \tau, X, \lambda)/\partial T$ is obtained by differentiating (19) with respect to dimensionless time variable T, with the result given in Appendix B. Therefore the small-perturbation solution (17) to the stochastic partial differential equation (15) is now complete. Since analytical evaluation of the integrals in (17*b*) and (32) is not straightforward, numerical integration techniques must be employed.

Equation (32) represents the general result so that any autocovariance function of $R'(X)$ can be employed. However, in this work the fluctuation of the retardation factor about its mean value $\langle R \rangle$ is considered to be characterized by the commonly used exponential autocovariance function

$$C_{R'}(X_i, X_j) \equiv E[R'(X_i) R'(X_j)] = \sigma_{R'}^2 \exp[-|X_i - X_j|] \tag{33}$$

where $\sigma_{R'}^2$ is the variance of $R'(X)$.

NUMERICAL METHODOLOGY

In order to verify the small-perturbation solution, a numerical approximation to the transport model has been developed, so that model simulations obtained by the two different solution procedures can be compared. The advection-dispersion partial differential equation with spatially variable retardation factor (11) is approximated numerically, for a step or continuous solute injection ($T_p \to \infty$), by the well-known finite difference scheme of *Crank and Nicolson* [1947]. The variable retardation factor at each discrete nodal point is evaluated by

$$R_i = \langle R \rangle + R_i' \tag{34}$$

where R_i' is the zero-mean random fluctuation of $\langle R \rangle$ at node i. These fluctuations are obtained by the Markovian generating scheme [*Fiering and Jackson*, 1971]

$$R_{i+1}' = rR_i' + e_i[\sigma_{R'}^2(1 - r^2)]^{1/2} \tag{35}$$

where the e_i are independent standard normal sampling variates with zero mean and unity standard deviation and r is the lag-one serial correlation coefficient defined by

$$r = \exp[-\Delta X] \tag{36}$$

where ΔX is the uniform spatial grid size. Equation (35) is appropriate when the exponential autocovariance model of (33) is used.

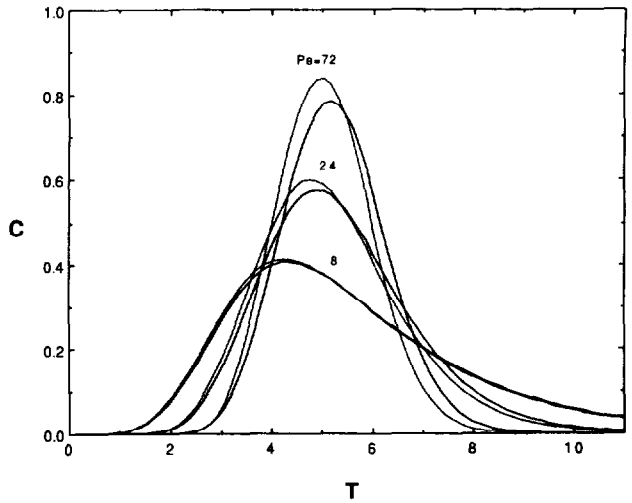

Fig. 1. Breakthrough curves at several values of Pe for solute transport with spatially variable (solid lines) and invariant (dotted lines) retardation factor, representing the system response to a broad pulse solute injection ($\langle R \rangle = 1.8$, $T_p = 2$, $X = 0.83$, and $\sigma_{R'}^2 = 0.1$).

DISCUSSION

We have studied the problem of transport of sorbing solutes in a porous medium which is heterogeneous with respect to partition coefficients. This problem has similarities to the extensively studied case of transport in a medium with variable advective velocity, caused by heterogeneity with respect to hydraulic conductivity [e.g., *Gelhar and Axness*, 1983]. In either case, the rate of transport of a solute "particle" varies with its location. The presence of high and low mobility zones results in an increase in the rate of dispersive flux.

Using the analytical small-perturbation solution to the one-dimensional advection-dispersion equation with spatially variable retardation factor, we have simulated concentration histories for several values of Pe. The integrals in (17*b*) and (32) have been evaluated numerically by the extended Simpson's rule [*Press et al.*, 1986]. Figures 1 and 2 illustrate the effect of the spatially variable retardation factor

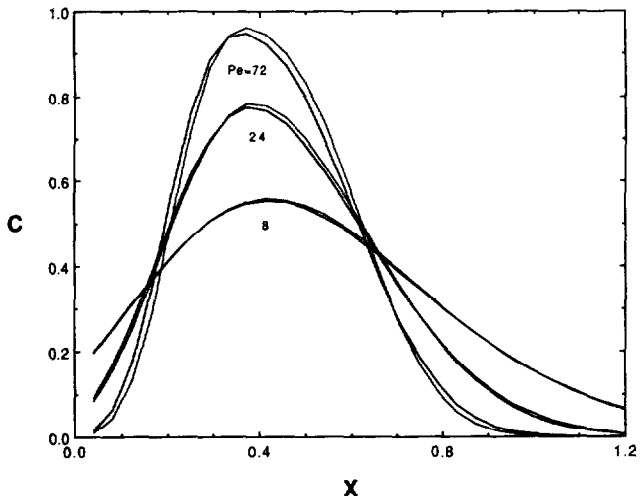

Fig. 2. Solute concentration snapshots at several values of Pe for transport with spatially variable (solid lines) and invariant (dotted lines) retardation factor, representing the system response to a broad pulse solute injection ($\langle R\rangle = 1.8$, $T_p = 2$, $T = 3$, and $\sigma^2_{R'} = 0.1$).

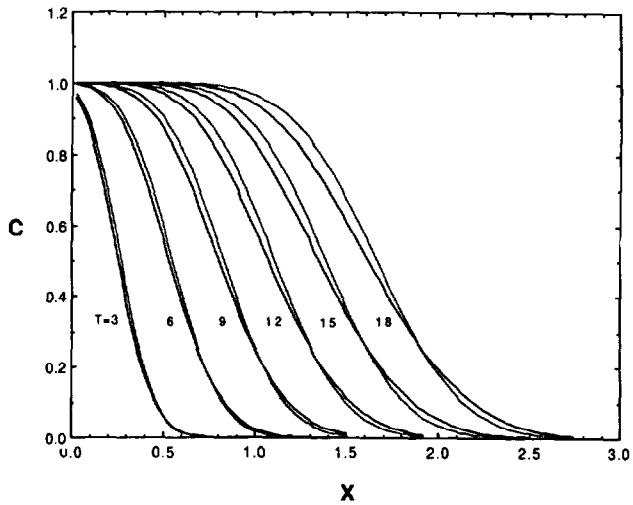

Fig. 3. Breakthrough curves plotted, at various points in time, for solute transport with spatially variable (solid lines) and invariant (dotted lines) retardation factor, representing the system response to a step or continuous solute injection ($Pe = 24$, $\langle R\rangle = 1.8$, and $\sigma^2_{R'} = 0.1$).

at several values of Pe, for solute concentration profiles distributed through time (breakthrough curve) and space (snapshot of solute concentration), respectively, by comparison with the advection-dispersion equation with constant coefficients. These illustrations indicate that the impact of spatially variable retardation increases with increasing Pe. This result was expected because an increase in Pe implies an increase in l. Furthermore, Figures 1 and 2 suggest that the variable retardation leads to a decrease in solute mobility; the movement of the center of mass is delayed. This may not be true at large values of time, an issue which is currently being investigated by the method of moments. It should be noted that the areas under the curves corresponding to constant and variable retardation are not necessarily equal. The reason is that, as the solute samples all locations through a one-dimensional porous medium with spatially variable retardation, the mass sorbed onto sites with $R'(X) \leq 0$ plus the mass sorbed onto sites with $R'(X) > 0$ may not equal the mass sorbed in an equivalent system with constant retardation $\langle R\rangle$. The zeroth moment of spatially distributed solute concentration data is a measure of the total mass in solution at a given time and is defined as

$$m_0(T) = \int_0^\infty C(T, X)\, dX \tag{37}$$

Integrating with respect to X equations (11) and (15), and employing the appropriate initial and boundary conditions for the integral-limit evaluation lead to the following zeroth moments:

$$m_0(T)_a = \frac{T_p}{\langle R\rangle} \tag{38}$$

$$m_0(T)_b = \frac{T_p}{\langle R\rangle} - \int_0^{T_p} d\tau \int_0^\infty \left\langle \frac{R'(\lambda)}{\langle R\rangle} \frac{\partial C'(\tau, \lambda)}{\partial \tau} \right\rangle d\lambda \tag{39}$$

where $T \geq T_p$, and subscripts a and b indicate the cases of homogeneous ($R(X) = \langle R\rangle$) and heterogeneous ($R(X) = \langle R\rangle + R'(X)$) retardation, respectively. For large times ($T \to \infty$), in view of (32), the second term on the right-hand side of (39) vanishes. Therefore, asymptotically, the mass in solution predicted by the two zeroth moments is essentially identical. At early times, $m_0(T)_b$ could be fluctuating about the value of $m_0(T)_a$. These fluctuations are caused by the liquid phase solute concentration changes associated with the movement of early time concentration profiles through regions of increasing/decreasing retardation. For example, the total mass in solution of a steep concentration front will be lower if it moves through a region of decreasing retardation than a region of increasing retardation. However, at late times when the solute plume is much larger than the integral scale of $R'(X)$, so that the solute concentration in solution can be considered position-independent constant, it is easy to verify that the total mass in the liquid phase is the same as if the spatial variability of retardation were neglected. It may not be unrealistic to expect that at large times the effects of the spatially variable retardation can be simulated by the classical advection-dispersion equation with constant "effective" coefficients. However, justification of such an assumption, and furthermore, attainment of the required adjustments in the coefficients of the advection-dispersion equation, demands a better investigational procedure than visual inspection. Such analysis will not be attempted in this work.

The response of the system to a step or continuous solute injection ($T_p \to \infty$), at several points in time, is illustrated in Figure 3. The impact of spatially variable retardation on the simulated behavior of solute transport is shown to be dependent on the distance traveled from the upstream boundary. Careful inspection of Figure 3 reveals that solute spreading is increased. The enhancement of solute spreading depends critically on the correlation scale and variance of $R'(X)$. The prominent effect of the variance in the retardation factor is shown in Figure 4. An increase in $\sigma^2_{R'}$ expands the spreading of the solute front. The broadening of the predicted solute

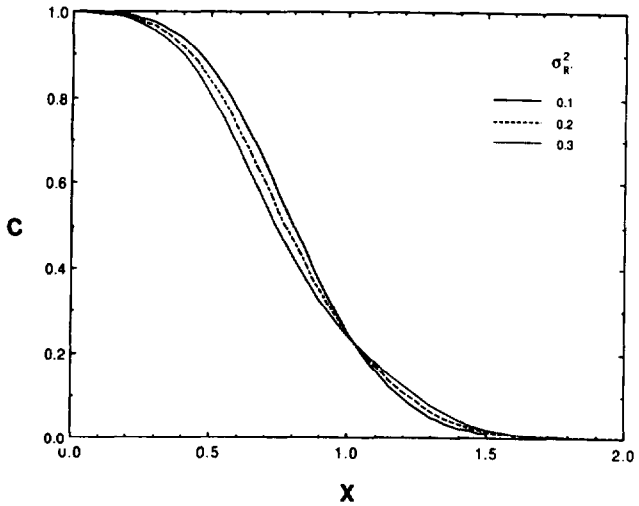

Fig. 4. Effect of $\sigma^2_{R'}$ in temporally distributed solute concentrations profiles (Pe = 24, $\langle R \rangle$ = 1.8, and T = 1.5).

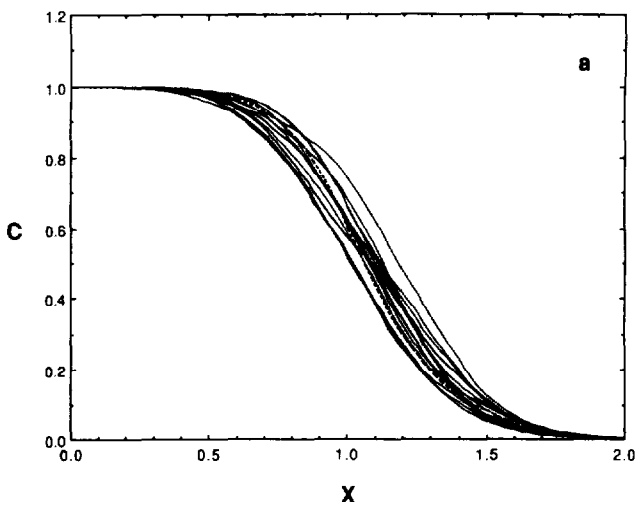

Fig. 5*a*. Numerical approximations for several realizations of the spatial distribution of $R'(x)$.

concentration curves is influenced by an enhancement of the dispersive flux. Therefore, by increasing the spatial variability of retardation, the transport model becomes more of the parabolic type, and predictions of solute concentration histories present more extended tailing. This effect is analogous to the increase in dispersivity caused by an increase in the variability of hydraulic conductivity [e.g., *Gelhar et al.*, 1979; *Smith and Schwartz*, 1980].

The analytical solution derived in this paper describes the dependence of ensemble mean solute concentration on statistical parameters of the retardation random process. In other words, the analytical small-perturbation solution is based on the average of individual realizations of the spatial distribution of retardation factor. The numerical approximation, however, depends on individual realizations of spatially discretized retardation values. The numerical approximation has been developed only for verification purposes. To compare the analytical small-perturbation solution to the numerical approximation, it is necessary to obtain several numerical simulations based on different realizations. The average of a large number of such numerical simulations should be identical to the response predicted by the analytical small-perturbation solution. Figure 5*a* presents 15 numerical simulations based on different realizations of the spatial variation of $R'(X)$. As a verification exercise, the estimate of the ensemble mean response based on the 15 numerical simulations is plotted in Figure 5*b* together with the breakthrough curve obtained by the small-perturbation solution. The two predictions clearly agree closely. For the special case of $R'(X) = 0$, in view of (17*c*), the first term on the right-hand side of (17*b*) vanishes. Furthermore, $F(T, X, 0)$ (defined in (19)) multiplied by $\Psi(T, 0)$ (defined in (17*d*)) is identical to $\Omega(T, X)$ (defined in (31)). Since $\Omega(T, X)$ is the derivative of $\langle C_0 \rangle(T, X)$ with respect to T, the expression (17) reduces to the familiar solution of the advection-dispersion equation with constant coefficients (24).

The physical significance of the synthetic experiments presented may be criticized because there is a dearth of experimental results to support the validity of the autocovariance function used. Actually, *Durant and Roberts* [1986] reported that the vertical distribution of $K_d(x)$ for organic solute sorption on Borden aquifer material is not well described by an exponential function; instead a combination of spherical/linear model was suggested. However, it should be noted that the fundamental results of this study will not be affected qualitatively if another autocovariance function had been used. Although an exponential autocovariance function is assumed to represent the spatial structure of the retardation factor fluctuations, any other function can easily be employed in (32).

SUMMARY

The primary contribution of this work is the development of an analytical small-perturbation solution to the stochastic advection-dispersion partial differential equation that relates the ensemble solute concentration to the statistics of a stationary retardation factor. The solution is derived for a one-dimensional semi-infinite porous medium with a flux-type inlet boundary condition, under the assumption that

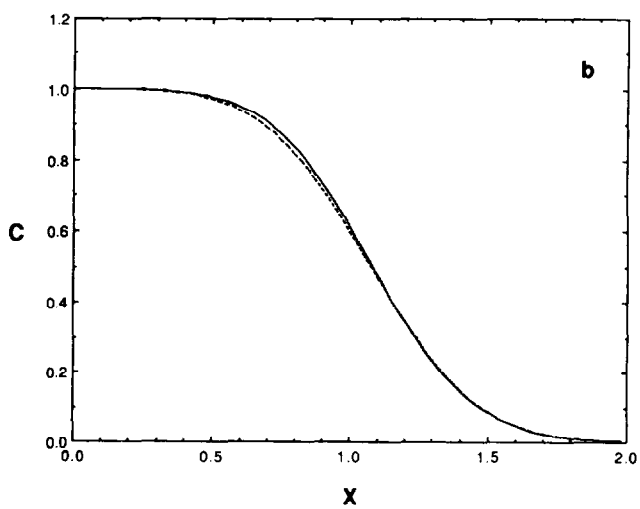

Fig. 5*b*. Comparison between analytical solution (dashed line) and numerically estimated ensemble mean response (solid line) (Pe = 24, T = 12, and $\sigma^2_{R'}$ = 0.1).

sorption is governed by a linear equilibrium isotherm. Any applicable autocovariance function can be employed to describe the spatially distributed fluctuations of the retardation factor.

We have demonstrated through synthetic examples that spatially variable retardation affects the transport of sorbing but otherwise nonreacting solutes in homogeneous porous media. Comparing the advection-dispersion equation with constant coefficients demonstrates that at early times the center of mass moves more slowly in the variable retardation case and the impact of spatially variable retardation increases with increasing Pe. At larger values of time, when the travel distance is much larger than the correlation scale of the retardation factor, the zeroth moment for the variable retardation case is identical to the case where the spatial variability of retardation is neglected. Furthermore, an increase in σ_R^2 yields an increase in spreading of the solute front. The impact of spatially variable retardation is expected to become significantly more pronounced if $R(x)$ is allowed to vary several orders of magnitude and the Péclet number is large. However, such cases have not been examined in the results shown in this work because of the limitations of the small-perturbation technique employed and inaccuracy of the numerical method used for comparison. Good agreement was shown between the average of several numerically calculated realizations of the spatially distributed fluctuations of the retardation factor, and the analytical small-perturbation solution.

APPENDIX A: DERIVATION OF THE $F(T, X, \xi)$ FUNCTION

The function $F(T, X, \xi)$ is the solution to the problem described by the following partial differential equation and initial boundary conditions:

$$\langle R\rangle \frac{\partial F(T, X, \xi)}{\partial T} = \frac{1}{Pe}\frac{\partial^2 F(T, X, \xi)}{\partial X^2} - \frac{\partial F(T, X, \xi)}{\partial X} \qquad (A1a)$$

$$0 \le X < \infty$$

$$F(0, X, \xi) = \delta(X - \xi) \qquad (A1b)$$

$$-\frac{1}{Pe}\frac{\partial F(T, 0, \xi)}{\partial X} + F(T, 0, \xi) = 0 \qquad (A1c)$$

$$\frac{\partial F(T, \infty, \xi)}{\partial X} = 0 \qquad (A1d)$$

The solution is obtained with the methods of *Lindstrom and Boersma* [1971], and *Chrysikopoulos et al.* [1990]. Taking Laplace transforms with respect to time variable T and space variable X leads to the following set of algebraic equations:

$$\langle R\rangle[s\tilde{F}(s, \gamma, \xi) - \tilde{F}(0, \gamma, \xi)] = \frac{1}{Pe}[\gamma^2\tilde{F}(s, \gamma, \xi) - \gamma\tilde{F}(s, 0, \xi) - \tilde{F}_x(s, 0, \xi)] - [\gamma\tilde{F}(s, \gamma, \xi) - \tilde{F}(s, 0, \xi)] \qquad (A2a)$$

$$\tilde{F}(0, \gamma, \xi) = e^{-\gamma\xi} \qquad (A2b)$$

$$-\tilde{F}_x(s, 0, \xi) + Pe\,\tilde{F}(s, 0, \xi) = 0 \qquad (A2c)$$

$$\tilde{F}_x(s, \infty, \xi) = 0 \qquad (A2d)$$

where

$$\tilde{F}(s, \gamma, \xi) = \int_0^\infty \int_0^\infty F(T, X, \xi)\, e^{-sT} e^{-\gamma X}\, dX\, dT \qquad (A3)$$

the "tilde" signifies Laplace transform, and s, γ are the Laplace domain time and space variables, respectively. Substituting initial condition (A2b) into (A2a), employing boundary condition (A2c), and solving for $\tilde{F}(s, \gamma, \xi)$ yields

$$\tilde{F}(s, \gamma, \xi) = \frac{\gamma\tilde{F}(s, 0, \xi) - Pe\,\langle R\rangle e^{-\gamma\xi}}{(\gamma + M - N)(\gamma + M + N)} \qquad (A4)$$

where

$$M = -\frac{Pe}{2} \qquad (A5)$$

$$N = \left(Pe\langle R\rangle s + \frac{Pe^2}{4}\right)^{1/2} \qquad (A6)$$

Using Laplace transforms from the tabulation of *Roberts and Kaufman* [1966] and employing the convolution theorem, the inverse of (A4) with respect to γ is determined to be

$$\tilde{F}(s, X, \xi) = \tilde{F}(s, 0, \xi)\frac{-(M - N)e^{-(M-N)X} + (M + N)e^{-(M+N)X}}{2N} - \frac{Pe\,\langle R\rangle[e^{-(M-N)(X-\xi)} - e^{-(M+N)(X-\xi)}]}{2N} \qquad (A7)$$

Applying boundary condition (A2d) in (A7), and taking the limit $x \uparrow \infty$, $\tilde{F}(s, 0, \xi)$ is evaluated to be

$$\tilde{F}(s, 0, \xi) = \frac{-Pe\,\langle R\rangle}{(M - N)} e^{(M-N)\xi} \qquad (A8)$$

Substituting (A8) into (A7) yields

$$\tilde{F}(s, X, \xi) = \frac{Pe\,\langle R\rangle}{2N} e^{-(M+N)(X-\xi)} - \frac{Pe\,\langle R\rangle(M + N)}{2N(M - N)} e^{-M(X-\xi)} e^{-N(X+\xi)} \qquad (A9)$$

Resubstituting (A5) and (A6) into (A9), inversion from Laplace time variable s to real dimensionless time T is straightforward, and all necessary transforms can be found in the tabulation of *Roberts and Kaufman* [1966]. The Laplace inversions for each term on the right-hand side of (A9) are given by the following expressions:

$$L^{-1}\left\{\frac{e^{-(M+N)(X-\xi)}}{N}\right\} = \left(\frac{1}{Pe\,\langle R\rangle\pi T}\right)^{1/2} \cdot \exp\left[\frac{Pe(X - \xi)}{2}\right]\exp\left[-\frac{Pe\,\langle R\rangle(X - \xi)^2}{4T} - \frac{Pe\,T}{4\langle R\rangle}\right] \qquad (A10)$$

$$L^{-1}\left\{\frac{Me^{-M(X-\xi)}\,e^{-N(X+\xi)}}{N(M - N)}\right\} = \frac{1}{2\langle R\rangle}\exp[Pe\,X]$$

$$\cdot \operatorname{erfc}\left[\left(\frac{Pe\ T}{4\langle R\rangle}\right)^{1/2}+\left(\frac{Pe\ \langle R\rangle}{4T}\right)^{1/2}(X+\xi)\right] \tag{A11}$$

$$L^{-1}\left\{\frac{e^{-M(X-\xi)}\ e^{-N(X+\xi)}}{M-N}\right\}=-\left(\frac{1}{Pe\ \langle R\rangle \pi T}\right)^{1/2}$$
$$\cdot\exp\left[\frac{Pe(X-\xi)}{2}\right]\exp\left[-\frac{Pe\ \langle R\rangle(X+\xi)^2}{4T}-\frac{Pe\ T}{4\langle R\rangle}\right]$$
$$+\frac{1}{2\langle R\rangle}\exp\left[Pe\ X\right]\operatorname{erfc}\left[\left(\frac{Pe\ T}{4\langle R\rangle}\right)^{1/2}+\left(\frac{Pe\ \langle R\rangle}{4T}\right)^{1/2}(X+\xi)\right] \tag{A12}$$

where L^{-1} is the Laplace inverse operator. Utilizing (A10)–(A12) in (A9) leads to

$$F(T, X, \xi)=\left(\frac{Pe\ \langle R\rangle}{4\pi T}\right)^{1/2}\exp\left[\frac{Pe(X-\xi)}{2}\right]$$
$$\cdot\exp\left[-\frac{Pe\ \langle R\rangle(X-\xi)^2}{4T}-\frac{Pe\ T}{4\langle R\rangle}\right]$$
$$+\left(\frac{Pe\ \langle R\rangle}{4\pi T}\right)^{1/2}\exp\left[\frac{Pe(X-\xi)}{2}\right]$$
$$\cdot\exp\left[-\frac{Pe\ \langle R\rangle(X+\xi)^2}{4T}-\frac{Pe\ T}{4\langle R\rangle}\right]-\left(\frac{Pe}{2}\right)\exp\left[Pe\ X\right]$$
$$\cdot\operatorname{erfc}\left[\left(\frac{Pe\ T}{4\langle R\rangle}\right)^{1/2}+\left(\frac{Pe\ \langle R\rangle}{4T}\right)^{1/2}(X+\xi)\right] \tag{A13}$$

APPENDIX B: PARTIAL DERIVATIVE OF $F(T-\tau, X, \lambda)$ WITH RESPECT TO T

$$\frac{\partial F(T-\tau, X, \lambda)}{\partial T}=-\left\{\left(\frac{Pe\ \langle R\rangle}{16\pi(T-\tau)^3}\right)^{1/2}\right.$$
$$\left.+\left(\frac{Pe\ \langle R\rangle}{4\pi(T-\tau)}\right)^{1/2}\left(\frac{Pe}{4\ \langle R\rangle}\right)\right\}$$
$$\cdot\exp\left[\frac{Pe\ (X-\lambda)}{2}-\frac{Pe(T-\tau)}{4\langle R\rangle}\right]$$
$$\cdot\left\{\exp\left[-\frac{Pe\ \langle R\rangle(X-\lambda)^2}{4(T-\tau)}\right]+\exp\left[-\frac{Pe\ \langle R\rangle(X+\lambda)^2}{4(T-\tau)}\right]\right\}$$
$$+\left(\frac{Pe\ \langle R\rangle}{4\pi(T-\tau)}\right)^{1/2}\exp\left[\frac{Pe(X-\lambda)}{2}-\frac{Pe(T-\tau)}{4\langle R\rangle}\right]$$
$$\cdot\left\{\frac{Pe\ \langle R\rangle(X-\lambda)^2}{4(T-\tau)^2}\exp\left[-\frac{Pe\langle R\rangle(X-\lambda)^2}{4(T-\tau)}\right]\right.$$
$$\left.+\frac{Pe\langle R\rangle(X+\lambda)^2}{4(T-\tau)^2}\exp\left[-\frac{Pe\langle R\rangle(X+\lambda)^2}{4(T-\tau)^2}\right]\right\}$$
$$-\left(\frac{Pe}{2}\right)\left(\frac{Pe^{1/2}\langle R\rangle(X+\lambda)-Pe^{1/2}(T-\tau)}{2(\pi\langle R\rangle)^{1/2}(T-\tau)^{3/2}}\right)\exp\left[Pe\ X\right]$$
$$\cdot\exp\left[-\frac{[Pe^{1/2}(T-\tau)+Pe^{1/2}\langle R\rangle(X+\lambda)]^2}{4\langle R\rangle(T-\tau)}\right] \tag{B1}$$

where the following expression has been employed:

$$\frac{d}{dz}\operatorname{erfc}[z]=-\frac{2}{\pi^{1/2}}\exp[-z^2] \tag{B2}$$

NOTATION

- c liquid phase solute concentration (solute mass/liquid volume), M/L^3.
- c_p pulse-injected solute concentration, M/L^3.
- c^* solid phase concentration of sorbed solute (solute mass/solids mass), M/M.
- C dimensionless liquid phase solute concentration.
- $\langle C\rangle$ expected value of the dimensionless liquid phase solute concentration.
- C' zero-mean random fluctuation of $\langle C\rangle$.
- D hydrodynamic dispersion coefficient, L^2/t.
- e_i standard normal variates: $N(0, 1)$.
- $E[\ ]$ expectation.
- $\operatorname{erfc}[x]$ complementary error function, equal to $1-(2/\pi^{1/2})\int_0^x e^{-z^2}\,dz$.
- K_d partition or distribution coefficient (liquid volume/solid mass), L^3/M.
- l correlation scale, L.
- L^{-1} Laplace inverse operator.
- m_0 zeroth spatial moment.
- Pe Péclet number.
- r lag-one serial correlation coefficient.
- R spatially variable retardation factor.
- $\langle R\rangle$ expected value of the retardation factor.
- R_i R value at node i.
- R' zero-mean random fluctuation of $\langle R\rangle$.
- R_i' R' value at node i.
- s Laplace transform variable.
- t time, T.
- t_p duration of the solute pulse, T.
- T dimensionless time.
- T_p dimensionless duration period of solute pulse.
- U average interstitial velocity, L/t.
- x spatial coordinate in the direction of flow, L.
- X dimensionless length.
- γ Laplace transform variable.
- $\delta(\ )$ Dirac delta function.
- ΔX size of uniform spatial grid.
- ε mathematical artifice, scalar.
- θ porosity (liquid volume/aquifer volume), L^3/L^3.
- ρ bulk density of the solid matrix (solid mass/aquifer volume), M/L^3.
- λ, ξ integration variables.
- $\sigma_{R'}^2$ variance of R'.
- τ integration variable, T.

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