

# Stochastic-perturbation analysis of solute transport through porous media with spatially variable retardation factor

Vladimir Alvarado

PDVSA Intevep., Apartado 76343, Caracas 1070A, Venezuela

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## Abstract

A closed-form first-order solution to the Laplace transform of the convection-dispersion equation is derived for sorbing or partitioning tracers under conditions of chemical equilibrium. For the given flux boundary condition, the Laplace transform of the transit-time distribution,  $P(t)$ , is found for retardation factors,  $R$ , owing an exponentially decaying covariance function. Moments of  $P(t)$ ,  $\langle t^n \rangle$ , are obtained by taking derivatives of  $\tilde{P}(S) = L\{P(t)\}$ , which means that  $\tilde{P}(S)$  is a generator of moments. These moments are employed to find transport coefficients, in particular the so-called dispersion coefficient,  $D$ . The main effect of the variable  $R$  is to enhance the spreading of the sorbing tracer, that increases the value of  $D$ . At late times (large distances), the first-order moment is expected to be insensitive to the spatial variation of  $R$ . Thus, the mean velocity of a traveling pulse becomes independent of these variations, unless an infinite correlation length is imposed.

**Key words:** Absorption; dispersion; porous media.

## Ánalysis de perturbación estocástica del transporte de un soluto a través de un medio poroso con un factor espacial de retardación variable

### Resumen

Una solución analítica de la transformada de Laplace de la ecuación de convección-dispersión se deriva para trazadores que se absorben o participan en equilibrio químico. La transformada de Laplace de la distribución de tiempos de tránsito,  $P(t)$ , se encuentra para el caso de factores de retardo,  $R$ , que presentan una función de covarianza que decrece exponencialmente con la distancia. Momentos de  $P(t)$ ,  $\langle t^n \rangle$ , se obtienen al tomar derivadas de  $\tilde{P}(S) = L\{P(t)\}$ , es decir que  $\tilde{P}(S)$  es la función generadora de momentos. Coeficientes de transporte pueden hallarse a partir de los momentos, en particular el coeficiente de dispersión,  $D$ . El principal efecto de la variación espacial de  $R$  es el incrementar  $D$ . El primer momento resulta insensible a estas variaciones. Por lo tanto, la velocidad media de un pulso de trazadores es independiente de las variaciones de  $R$ , a menos que la longitud de correlación sea infinita.

**Palabras clave:** Absorción; dispersión; medio poroso.

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\* Autor para la correspondencia.

## I. Introduction

In recent years, great deal of effort has been dedicated to developing theories of groundwater solute transport. This has become an issue in contamination of groundwater resources given the stringent demands on water preservation (1). In the oil industry, the need for inexpensive reservoir characterization strategies has attracted attention to the area of well-to-well tracer tests (2). These two interests involve detailed description of the dispersion phenomenon. This phenomenon occurs when a solute spreads by the action of molecular diffusion and hydrodynamical convection. Chemical reaction and/or absorption tend to complicate the description of this transport process. For a linear reaction at equilibrium, the transport is expected to obey the convection-dispersion equation.

$$R \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} - U \frac{\partial c(x,t)}{\partial x} \quad [1]$$

where  $c$  is the mean concentration of the sorbing species,  $D$  is the local dispersion coefficient [scalar] and  $U$  is the mean or Darcy velocity of the fluid that carries the tracer.  $R$  is the so-called retardation factor. Typically, when a sharp concentration pulse of a chemical species in solution, e.g. a tracer, is injected into porous media, the interplay between convection and molecular diffusion causes the pulse to widen with time at a rate much higher than diffusion alone. The dispersion coefficient can be interpreted as an effective diffusion coefficient, whose character is usually tensorial [though only one component is treated here] and is strongly influenced by the velocity field in the media. Chemical reactions or processes that are modeled as such tend to increase the value of the dispersion coefficient.

Several authors have showed that spatial random variations of the retardation factor widen the transit-time distribution (3, 4),

hence increasing the spreading of a tracer. Sugita and Gillham proved that pore-level variations of the retardation factor can be responsible for a ten-fold increase in dispersion (5, 6). An example from the fractured media literature is the work of Wels and Smith (7).

In this article, a first-order perturbation analysis is carried out to study the effect of spatially variable retardation factors on the dispersion of sorbing tracers, by the determination of moments of the transit-time distribution in a one-dimensional medium. This paper is divided in 4 sections. First, an introduction of the problem is given, followed by the derivation of the first-order perturbation analysis for the convection-dispersion equation; the Laplace transform of the resulting equations is taken to obtain the evolution equation for the generator of moments; two transport coefficients are derived from the moment analysis: the mean velocity and the dispersion coefficient. Some results are shown to illustrate the use of the stochastic perturbation method. Finally, the conclusions are drawn.

## II. First-order perturbation analysis

The starting point for this perturbation analysis is the convection-dispersion equation with a retardation factor,  $xxx$ , that accounts for a first-order reversible chemical reaction at equilibrium. Chemical reactions of this type can reasonably model processes such as reversible sorption at the pore surface in a high dilution regime. The convection-dispersion equation, taken here in its one-dimensional form, is

$$R(x) \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} - U \frac{\partial c(x,t)}{\partial x} \quad [2]$$

$$\begin{aligned} c(x,t=0) &= 0 \left[ -D \frac{\partial c(x,t)}{\partial t} + U c(x,t) \right]_{x=0} \\ &= \delta(t); \quad c(x=L,t) = 0 \end{aligned}$$

In contrast with equation [1], the retardation factor changes with position in equation [2]. For the finite domain of length  $L$  considered here, the equation above can be written in dimensionless form as follows:

$$R(X) \frac{\partial C(X,T)}{\partial T} = \frac{1}{Pe} \frac{\partial^2 C(X,T)}{\partial X^2} - \frac{\partial C(X,T)}{\partial C} \quad [3]$$

where  $Pe = \frac{UL}{D}$ ;  $X = \frac{x}{L}$ ;  $T = \frac{tU}{L}$ . The concentration was made dimensionless by choosing a reference concentration value.

In equation [3],  $Pe$  is the Peclet number. In case semi-infinite media are considered, another length scale should be selected to make the equations unit-free. To proceed with the stochastic-analysis, the concentration is split in a mean value,  $\langle C \rangle$ , and a stochastic term,  $C'$  originated in spatial variations of the retardation factor.

$$C(X,T) = \langle C \rangle(X,T) + C'(X,T) \quad [4]$$

$$R'(X) = \langle R \rangle(X) + R'(X)$$

It is assumed that  $\langle R' \rangle = \langle C' \rangle = 0$  which means that  $C$  and  $R$  are stationary variables. Expressions in [4] are replaced in equation [3], and the ensemble average taken to obtain:

$$\langle R \rangle \frac{\partial \langle C \rangle}{\partial T} - \frac{1}{Pe} \frac{\partial^2 \langle C \rangle}{\partial X^2} + \frac{\partial \langle C \rangle}{\partial X} = - \left\langle R' \frac{\partial C'}{\partial T} \right\rangle \quad [5]$$

No approximation has been introduced so far. The right-hand side of equation [5] represents a source term for the mean concentration equation. The problem of the perturbation analysis is to find a closed-form for the source term by carrying out a series expansion with respect to the stochastic parameter, that is the retardation factor. Here, only zeroth-and first-order are kept.

$$R'(X) = \varepsilon^1 R_1(X)$$

$$C'(X,T) = \varepsilon^1 C_1'(X,T) + \dots \quad [6]$$

$$\langle R \rangle = \varepsilon^0 \langle R_0 \rangle$$

$$\langle C \rangle(X,T) = \varepsilon^0 \langle C_0 \rangle(X,T) + \varepsilon^1 \langle C_1 \rangle(X,T) + \dots$$

The set of expressions in [6] is introduced into [5] to yield the approximate transport equations. The next step in the analysis is to separate contributions of different orders in the parameter  $\varepsilon$  ( $\varepsilon$  at the end is made equal to one). The zeroth-order contribution corresponds to the solution to the transport equation with constant coefficients:

$$\langle R_0 \rangle \frac{\partial \langle C_0 \rangle(X,T)}{\partial T} = \frac{1}{Pe} \frac{\partial^2 \langle C_0 \rangle(X,T)}{\partial X^2} - \frac{\partial \langle C_0 \rangle(X,T)}{\partial X} \quad [7]$$

Factoring out terms proportional  $\varepsilon^1$  yields the first-order equation:

$$\begin{aligned} \langle R_0 \rangle \frac{\partial \langle C_1 \rangle(X,T)}{\partial T} + \langle R_0 \rangle \frac{\partial C_1(X,T)}{\partial T} + R_1 \frac{\partial \langle C_0 \rangle(X,T)}{\partial T} \\ + \frac{1}{Pe} \frac{\partial^2 \langle C_1 \rangle(X,T)}{\partial X^2} + \frac{1}{Pe} \frac{\partial^2 C_1(X,T)}{\partial X^2} \\ - \frac{\partial \langle C_1 \rangle(X,T)}{\partial X} - \frac{\partial C_1(X,T)}{\partial X} \end{aligned} \quad [8]$$

What has to be showed now is that the evolution equation for  $\langle C_1 \rangle$  is not relevant for the remaining calculations. It is readily know that  $\langle C_1 \rangle = 0$  because the equation for  $\langle C_1 \rangle$  has no source terms, and the boundary conditions and initial conditions for  $\langle C_1 \rangle$  are all zero. With this, the equation for  $C_1$  is

$$\begin{aligned} \langle R_0 \rangle \frac{\partial C_1(X,T)}{\partial T} - \frac{1}{Pe} \frac{\partial^2 C_1(X,T)}{\partial X^2} + \frac{\partial C_1(X,T)}{\partial X} = \\ - R_1(X) \frac{\partial \langle C_0 \rangle(X,T)}{\partial T} \end{aligned} \quad [9]$$

The right-hand side of equation [9] acts as the source term in the evolution equation for the stochastic contribution to concentration. As in the article by Alvarado *et al.* (9), expressions for the transit-time distribution moments are developed. However, breakthrough curves and concentration profiles can be determined, if desired, by numerically inverting the solution back into the time domain. The generator of moments is obtained by taking the Laplace transform of the concentration evolution equations.

### Moments of the Transit-time Distribution

The transit-time distribution is given here by  $P(T) = -\left.\frac{\partial C(X,T)}{\partial X}\right|_{X=1}$  as the boundary conditions of the problem are

$\left.\frac{\partial \tilde{C}(X,T)}{\partial X}\right|_{X=0} = \delta(T)$  and  $C(X=1,T) = 0$  The

Laplace transform of  $P(T)$ ,  $\tilde{P}(S) = L\{P(T)\}$ , is the generator of moments. In essence, by solving the Laplace transform of the transport equation with respect to time, one can determine  $\tilde{P}(S)$  at any order with respect to the perturbation parameter by taking derivatives of  $C(X)$  at  $X=1$ . If all the moments of the transit-time distribution are computed, then a complete set of moments suffices to have a complete history of the tracer transport. The assumption is that all moments are well defined and finite. The zeroth-order equation is given by expression [7]. Its Laplace transform corresponds to:

$$\frac{\partial^2 \langle \tilde{C}_0 \rangle}{\partial X^2} - Pe \frac{\partial \langle \tilde{C}_0 \rangle}{\partial X} - Pe S \langle R_0 \rangle \langle \tilde{C}_0 \rangle = 0 \quad [10]$$

Equation [10] is subject to the initial and boundary conditions of the original problem, *i.e.*  $-\left.\frac{\partial \langle \tilde{C}_0 \rangle(X,S)}{\partial X}\right|_{X=0} = L\{\delta(T)\} = 1$ ,  $\langle \tilde{C}_0 \rangle(X,S)|_{X=1} = 0$  and  $\langle \tilde{C}_0 \rangle(X,T=0) = 0$  A combination of exponen-

tial functions (8, 9) leads to the following solution.

$$\langle \tilde{C}_0 \rangle = m e^{mX} \frac{(e^{-m_3(X-1)} - e^{m_3(X-1)})}{m \sinh m_3 + m_3 \cosh m_3} \quad [11]$$

where  $m_3 = \sqrt{m^2 + 2m\langle R_0 \rangle S}$ ;  $m = \frac{Pe}{2}$

The next order in the perturbation is found by solving for  $\tilde{C}_1$ . The Laplace transform of equation [9] gives

$$\frac{d^2 \tilde{C}_1}{dX^2} - Pe \frac{d\tilde{C}_1}{dX} - Pe \langle R_0 \rangle S \tilde{C}_1 = Pe R_1 S \langle \tilde{C}_0 \rangle \quad [12]$$

The solution to equation [12] is obtained by the standard Green function method for the Liouville's operator (10):

$$\tilde{C}_1(X,S) = \int_0^1 G(X,Z,S) f(Z,S) dZ \quad [13]$$

where  $G(X,Z,S)$  is the Green function and  $f(X) = Pe R_1 S \langle \tilde{C}_0 \rangle e^{-PeX}$ .  $G$  is the solution of the following problem:

$$\begin{aligned} \frac{d^2 G(X,Z)}{dX^2} - Pe \frac{dG(X,Z)}{dX} - Pe \langle R_0 \rangle S G(X,Z) &= \delta(X-Z) \\ -\left.\frac{1}{Pe} \frac{dG(X,Z)}{dX}\right|_{X=0} + G(X=0,Z) &= 0 \\ G(X=1,Z) &= 0 \end{aligned} \quad [14]$$

The Laplace transform of expression [5] is

$$\frac{d^2 \langle \tilde{C} \rangle}{dX^2} - Pe \frac{d\langle \tilde{C} \rangle}{dX} - \langle R \rangle S Pe \langle \tilde{C} \rangle = S Pe \langle R' C' \rangle \quad [15]$$

Equation [15] contains the covariance function between  $R'$  and  $C'$ , that is the source term sought in this analysis. Substitution of [13] into [15] completes the perturbed evolution equation.

$$\frac{d^2 \langle \tilde{C} \rangle}{dX^2} - Pe \frac{d \langle \tilde{C} \rangle}{dX} - \langle R \rangle S Pe \langle \tilde{C} \rangle = S Pe \int_0^1 G(X, Z, S) \langle R_1(X) R_1(Z) \rangle \langle \tilde{C}_0 \rangle(Z) e^{-PeZ} dZ \quad [16]$$

The only additional consideration to using the Green function is to take into account the inhomogeneous boundary condition given by the flux at the inlet boundary. This is easily overcome by splitting the solution as  $\langle \tilde{C} \rangle = v_1 + v_2$  where  $v_1$  is a solution that satisfies the equation with a source term, but has homogeneous boundary conditions, and where  $v_2$  holds the homogeneous differential equation with inhomogeneous boundary conditions. Thus,  $v_1$  is

$$v_1(X, S) = (PeS)^2 \int_0^1 G(X, Y) e^{-PeY} \left[ \int_0^1 G(Y, Z) \langle R(Y) R(Z) \rangle \langle \tilde{C}_0 \rangle(Z) e^{-PeZ} dZ \right] dY \quad [17]$$

$v_2$ , on the other hand, satisfies the same equation and boundary conditions as  $\langle \tilde{C}_0 \rangle$ , and hence it amounts to having the zeroth- ( $v_1$ ) and a first-order ( $v_2 = \langle \tilde{C}_0 \rangle$ ) terms. In the next section, the result of solving equation [17] is employed to evaluate the effect of  $R$  on spreading [the lengthy analytical result is not shown].

### III. Results

The perturbation solution of  $\tilde{P}(S)$  contains two separate contributions, and so do the moments. Henceforth, all moments can be written as follows:

$$\tilde{P}(S) = - \frac{1}{2m} \left( \frac{dv_1}{dX} + \frac{dv_2}{dX} \right)_{X=1}$$

$$\langle t^n \rangle = \left( \frac{\partial^n P_0}{\partial S^n} + \frac{\partial^n P_1}{\partial S^n} \right)_{S=0}$$

The subscripts indicate the order with respect to the perturbation. The first-order solution has a leading term proportional to  $S^2$ , as can be seen from equation [17]. This means that there are no contributions at

this order to the first moment of the transit-time distribution. In practice, the mean transit time should be insensitive to small spatial variations of the retardation factor, that is up to a first-order approximation. To evaluate predictions of the perturbation analysis, a finite-difference type of an approximation was implemented (11). The approximation requires sampling of the distribution of  $R$  for many realizations of disorder.

Figure [1 a] shows that  $\langle t \rangle$  indeed does not change with increasing values of

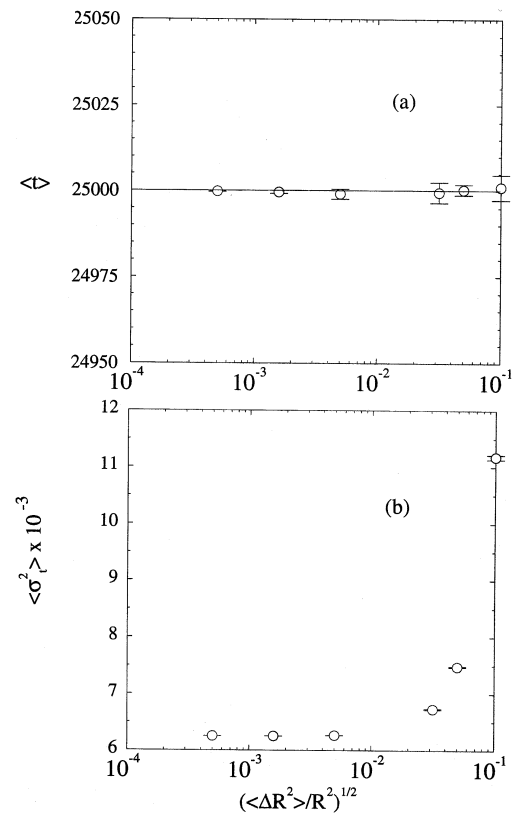


Figure 1.(a) Mean-transit time as a function of standard deviation of  $R$  (b)  $\langle \sigma_t^2 \rangle$  as a function of the standard deviation of  $R$ . The parameters are  $Ul/2D = 2.0$ ,  $\langle R \rangle = 2.0$ ,  $L/l = 5 \times 10^4$  and  $\xi = 10^{-4}$ . The error bars represent the standard deviation of  $10^3$  to  $10^4$  realizations.

$\langle (R)^2 \rangle$ . Thus, measurements of mean flow should be insensitive to this type of disorder. However, perturbation analysis shows that second- and higher-order moments are affected by spatial variations of the retardation factor. The variance,  $\sigma_t^2$ , was computed for the parameters employed in Figure [1a], as Figure [1b] shows. Large deviations from the lowest value of  $\sigma_t^2$  are observed, even for small values of  $\langle (R)^2 \rangle$ . The expression for the dispersion coefficient of the zeroth-order approximation in the limit of large Peclet numbers is (12):

$$\lim_{m \rightarrow \infty} D = \frac{1}{2R^2} \frac{U^3 \sigma_t^2}{L}$$

It should be noticed that small increments in the size of the perturbation causes considerable increments in the dispersion, that is 10% deviation from the mean value originates twice as much dispersion (when measured at zeroth order), as Figure (1b) indicates.

A comparison between the perturbative calculation and the numerical calculation is carried out in Figure (2). As can be seen, both the curves are very close and follow a straight line. This is expected at low values of  $\langle (R)^2 \rangle$ . The difference between the two curves can be attributed to higher-order corrections.

#### IV. Conclusions

A closed-form solution to the Laplace transform of the convection-dispersion equation for sorbing solutes was found under conditions of a spatially varying retardation factor. The solution yields the generator of moments. Moments of the transit-time distribution are affected by the spatial disorder in the retardation factor. As expected from the perturbation analysis, the first-order solution exhibits a linear contribution with respect to the variance of the retardation factor. The first moment of the distribution is nearly

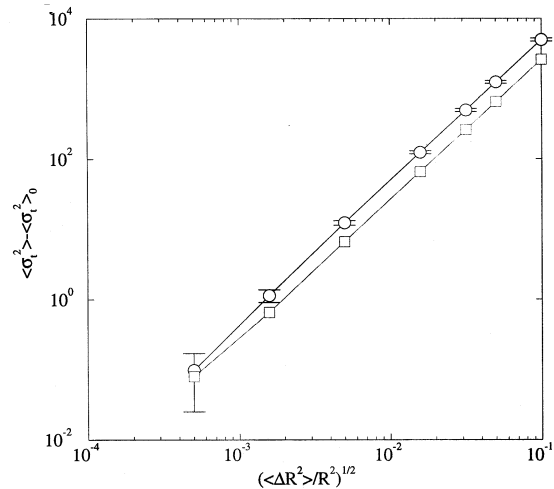


Figure 2. Curves were obtained by subtracting  $\langle \sigma_t^2 \rangle$  obtained with constant  $R$  from numerical and perturbative results. Parameters employed are  $U/D = 2$ ,  $\langle R \rangle = 2.0$ ,  $L/l = 5 \times 10^4$  and  $\xi = 10^{-4}$ . Circles indicate numerical solution, whereas squares refer to first-order approximation.

independent of  $\langle (R)^2 \rangle$ , but probably is affected by higher-order contributions.

The dispersion coefficient is enhanced by the distribution of  $R$ . The first-order solution leads to a dispersion coefficient that approximates better the local value of  $D$ . This suggests that experiments carried out with neutral tracers would give the right value of the dispersion coefficient, and if information on the distribution of  $R$  were known, then the transport would be correctly predicted. Perhaps the information on  $R$  could be accessed through imaging of rock samples, in the case of oil reservoirs.

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