

Discrete time- and length-averaged solutions of the advection-dispersion equation

Feike J. Leij and Nobuo Toride

U.S. Salinity Laboratory, Riverside, California

Abstract. Solute concentrations obtained from displacement experiments in porous media frequently represent discrete values as a result of averaging over a finite sampling interval. For example, effluent curves are made up of time-averaged concentrations while volume-averaged concentrations are obtained from core samples. The discrete concentrations are often described by continuous solutions of macroscopic solute transport equations such as the advection-dispersion equation (ADE). The continuous solution is often shifted to describe the average concentration. This paper compares continuous and time- or length-averaged solutions of the one-dimensional ADE cast in terms of flux-averaged and resident concentrations. Expressions for the time- and length-averaged concentrations are presented for solute applications described by Dirac delta or Heaviside functions (instantaneous and continuous releases of the solute) using four different combinations of solute application and detection modes. A temporal and spatial moment analysis was conducted to compare the traditional continuous description with the discrete time- or length-averaged approach. Graphical and tabular data are presented to evaluate the accuracy of continuous solutions of the ADE for determining transport parameters. Although significant errors may occur for extreme cases with low dispersion coefficients and large sampling intervals, shifting the continuous solution by half the sampling interval generally yields results similar to those obtained with the time- or length-averaged analysis. An advantage of averaged concentrations is that they permit greater flexibility to conduct experiments, since averaged concentrations provide an exact description of the data regardless of the sampling interval.

Introduction

Mathematical models are routinely employed in studies addressing the movement and fate of chemicals in porous media. The advection-dispersion equation (ADE) has been widely used to describe solute transport in porous media, although this equation is known to have certain limitations [Taylor, 1953; Dagan, 1989]. The ADE will be employed in this study for idealized conditions to derive analytical solutions for one-dimensional solute transport. Such solutions can be used for predicting solute concentrations over different temporal or spatial scales, for assessing the importance of various transport processes, or for estimating transport parameters.

The correctness of mathematical solutions for a theoretical transport problem depends on how well the boundary conditions and the concentration mode can be formulated compared to the actual experimental conditions. Frequently, we can not precisely describe transport in the physical system, particularly at arbitrary surfaces. Hence we will not consider the relative merits of different boundary conditions. Ample literature has been published on the use of first- and third-type inlet conditions in conjunction with flux- and volume-averaged concentrations for solute application to soil columns with a uniform initial distribution [Kreft and Zuber, 1978; Parker and van Genuchten, 1984a].

We are particularly interested in using the ADE, with a continuous dependent variable, to analyze (discrete) results

This paper is not subject to U.S. copyright. Published in 1995 by the American Geophysical Union.

Paper number 95WR00588.

from solute displacement experiments. Consider the description of an effluent curve from a column displacement experiment obtained with a fraction collector, where a new effluent sample is collected after an incremental sampling time Δt has expired [cf. van Genuchten and Wierenga, 1986]. Figure 1 demonstrates two possibilities to describe the (discrete) effluent concentration at the end of each sampling period ($\Delta t = 0.4$) for a hypothetical continuous concentration (solid line): (1) shift the curve and "sample" the effluent concentration halfway through the sampling interval, that is, at the centroid $t - 1/2\Delta t$ and (2) use an integrated (discrete) value $C_i(t)$ [e.g., Fischer et al., 1979] which serves as a running time average of the actual concentration of the sample. This paper is primarily concerned with exploring differences in describing solute concentrations with the (approximate) continuous and the (exact) discrete solutions; both are given as dashed lines in Figure 1. The shifted curve is continuous, while the time-averaged curve displays a discontinuity each time a new fraction is being collected; both curves will converge to the original continuous solution if $\Delta t \rightarrow 0$. The "observed" points of the shifted curve will normally be different from the time-averaged points, as shown in Figure 1, unless there is a strictly linear relationship between solute concentration versus time during each measurement interval. The distinction between the continuous and averaged solutions will become important for larger sampling times and for more nonlinear concentration curves (e.g., due to a variable input or initial distribution).

The concept of time-averaged concentrations, although fairly elementary, has received scant attention in the analysis of solute displacement experiments. Schnabel and Richie [1987]

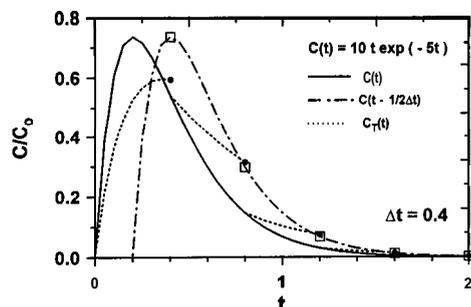


Figure 1. Schematic of averaged ($C_T(t)$) and shifted ($C(t - 1/2\Delta t)$) concentrations to describe effluent samples based upon a continuous solution of the advection-dispersion equation (ADE) ($C(t)$).

investigated the bias in estimated values of the dispersion coefficient D as a result of time assignments in the analysis of breakthrough curves. The experimental concentrations were described with a continuous solution, halfway or at the end of each sampling interval, and a discrete time-averaged value obtained through numerical integration. Optimizations based on the solutions halfway or at the end of the sampling interval produced values for D that differed up to 20 and 80%, respectively, from the actual value. Such studies could also be performed for discrete volume averaging.

There is a wide body of literature on averaging from the microscopic or pore scale, where parameters vary in an irregular manner with space and time, to the macroscopic scale, where parameters vary in a regular manner because they are averaged over many pores [Hassanizadeh and Gray, 1979; Cushman, 1986; Plumb and Whitaker, 1988; Dugan, 1989]. This averaging greatly simplifies the mathematical formulation of the problem by “filtering out” local physical phenomena. We will ignore such averaging entirely. Our analysis concerns the transformation from the macroscopic scale, where the concentration is continuous, to the sampling scale, where the concentration is discrete. In this case, transformation of the mathematical problem is typically not convenient because (1) the observation scale may vary in the course of an experiment (i.e., different sampling times or lengths), (2) the mathematical conditions are typically known in terms of continuous rather than discrete concentrations, (3) many solutions are already available for transport at the macroscopic scale (e.g., nonequilibrium or multidimensional transport), and (4) the results of experiments involving discrete concentrations are typically used in macroscopic transport models. Therefore we first solve the macroscopic problem and subsequently transform the dependent variable, the solute concentration, from the continuous to the discrete mode. We will examine discrete volume- and time-averaged concentrations for deterministic one-dimensional transport in homogeneous media. Since the area perpendicular to the flow direction is uniform, the volume averaging amounts to length averaging in our case.

Solute concentrations can be obtained with a wide variety of techniques. Hence it is important to have a comprehensive set of mathematical solutions suitable for different solute application and detection modes and for different averaging procedures. The first objective of this paper is to derive closed-form expressions for length- and time-averaged concentrations using a broad group of initial and boundary conditions involving instantaneous (Dirac delta) or continuous (Heaviside) func-

tions. A second objective is to investigate differences in solute concentrations, versus either depth or time, between solutions of the ADE based on continuous (shifted) and averaged descriptions. These differences will be quantified through moment analysis and curve fitting.

Analytical Expressions for Solute Concentrations

Averaging Procedures

The most widely used concept for the concentration is based on averaging the microscopic concentration over an averaging volume ΔV . The representative elementary volume (REV) is the averaging volume that is sufficiently large to eliminate bias as a result of microscale variations [cf. Bear and Verruijt, 1987]. Solute transport quantified with the resulting resident concentration C_R can be described with a continuum model such as the ADE. There is also an upper limit on the REV due to changes in macroscopic properties (spatial variability).

The flux-averaged or flowing concentration C_F is used for characterizing transport with velocity dependent injection and detection modes when the boundary conditions need to be given in terms of solute fluxes rather than resident concentrations [cf. Kreft and Zuber, 1986]. It is expressed as the ratio of the solute and solvent fluxes; for steady state one-dimensional flow this leads to [cf. Kreft and Zuber, 1978]

$$C_F = C_R - \frac{D}{v} \frac{\partial C_R}{\partial x} \quad (1)$$

where v is the pore water velocity and x denotes coordinate position. Differences between C_R and C_F are only substantial for a Peclet number below 5 [van Genuchten and Parker, 1984]. Similar to C_R , C_F is considered to be a continuous variable, but it is defined for a “representative elementary time interval”. Direct measurement of C_F is ordinarily not possible; C_F is primarily a mathematical entity whose value may actually be negative [Toride et al., 1993].

Time-averaged concentrations are obtained for a fixed position and can be defined by averaging a macroscopic concentration C over time according to

$$C_T(x, t_2; \Delta t) = \frac{1}{\Delta t} \int_{t_1}^{t_2} C(x, t) dt \quad \Delta t = t_2 - t_1 \quad (2)$$

The time-averaged concentration is a discrete variable with its value dependent upon the averaging period. Length-averaged values of a continuous concentration (C , and C_T) may be defined according to

$$C_L(x_2, t; \Delta x) = \frac{1}{\Delta x} \int_{x_1}^{x_2} C(x, t) dx \quad \Delta x = x_2 - x_1 \quad (3)$$

where x_1 and x_2 are the boundaries of the interval over which C is averaged (e.g., the sampling range) to obtain the discrete C_T . The dependency between averaging and averaged variable will, arbitrarily, be expressed at the end of the sampling interval. It is conceivable that a concentration is best expressed as both a spatial and a temporal average.

Solution of the ADE for Instantaneous and Continuous Solute Application

One-dimensional transport of a nonreactive solute species during steady flow can be modeled with the ADE as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (4)$$

Note that linear equilibrium solute transport could be readily described by including a retardation factor R [cf. *Jury and Roth, 1990*]. The concentration may be of the flux-averaged or resident type. Boundary and initial conditions are needed to augment the transport equation to obtain a complete formulation of the problem. The four sets of mathematical conditions used by *Kreft and Zuber [1978]* were applied to describe the continuous and instantaneous solute application to initially solute-free infinite and semi-infinite porous media. They elucidated the differences between these four combinations as a result of uniform (resident mode) and velocity dependent (flux mode) concentrations. Dispersion outside the medium is neglected, while the outlet condition will be defined at infinity for lack of a better condition; that is, the condition at the (physically) finite outlet is described with a mathematically infinite condition.

Following the work of *Kreft and Zuber [1978]*, Appendix A specifies solutions for a Heaviside or step input function, for (1) an infinite medium with injection (I) and detection (D) in the resident (R) mode, denoted by RI and RD, (2) an infinite medium with resident injection and flux (F) detection, i.e., RI and FD, (3) a semi-infinite medium with flux injection and resident detection, i.e., FI and RD, and (4) a semi-infinite medium with flux injection and flux detection, i.e., FI and FD. The fourth case also applies to resident application with detection in either the flux or resident mode. The mathematical problem has to be formulated in a consistent concentration mode; it is convenient to select the detection mode for this purpose. For example, if resident concentrations are measured with time domain reflectometry probes while the solute is applied at the top of a column with a pump (i.e., flux mode), the inlet condition needs to be reformulated in terms of a resident concentration. The initial and boundary conditions are also given in Appendix A. The customary subscripts to indicate the detection mode [cf. *Parker and van Genuchten, 1984b*] or the application and detection modes [*Kreft and Zuber, 1978*] have been omitted.

Expressions are given in Appendix A for the concentration as a function of (1) position and time, i.e., $C(x, t)$, also provided by *Kreft and Zuber [1978]*, (2) position and the temporal Laplace variable s , i.e., $\bar{C}(x, s)$, and (3) the spatial Fourier variable α or Laplace variable p and time, i.e., $\hat{C}(\alpha, t)$ or $\tilde{C}(p, t)$. Expressions in the complex domain may arise if integral transforms are used for the solution; they may be helpful for deriving time- or length-averaged concentrations as well as temporal and spatial moments. The Laplace and Fourier transforms are defined as

$$\mathcal{L}_t[C(x, t)] = \bar{C}(x, s) = \int_0^\infty C(x, t) \exp(-st) dt \quad (5)$$

$$\mathcal{L}_x[C(x, t)] = \tilde{C}(p, t) = \int_0^\infty C(x, t) \exp(-px) dx \quad (6)$$

$$\begin{aligned} \mathcal{F}[C(x, t)] &= \hat{C}(\alpha, t) \\ &= \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^\infty C(\xi, t) \exp(i\alpha\xi) d\xi \quad \xi = x - vt \quad (7) \end{aligned}$$

where $i^2 = -1$. Note that H denotes the Heaviside function in Appendix A, while the auxiliary variables are defined as follows:

$$a = v/(4D)^{1/2} \quad b = p(D)^{1/2} - a \quad k = x/D^{1/2} \quad (8)$$

Cases 1 and 2 concern infinite media where only application in the resident mode needs to be considered. A solution was obtained through transformation to the diffusion equation and subsequent solution with the Fourier transform. The solution for a resident injection and detection mode (case 1) is straightforward. For case 2 the resident initial condition was written in terms of the flux detection mode using (1) and $\partial H(x)/\partial x = \delta(x)$; the Dirac delta function $\delta(x)$ has the property

$$\int_{-\infty}^\infty m(x) \delta(x - x_0) dx = m(x_0) \quad (9)$$

where m may denote the total solute mass initially present at $x = x_0$.

Cases 3 and 4 concern semi-infinite media for which solutions can conveniently be obtained using Laplace transformation with respect to time and subsequent solution of the resulting ordinary differential equations. The inlet condition for case 3 needs to be reformulated to a third-type condition. An expression in the spatial Laplace domain, $\tilde{C}(p, t)$, can be obtained by applying (6) to the solution in the temporal Laplace domain, $\bar{C}(x, s)$, followed by Laplace inversion with respect to time using the transformation pair

$$\begin{aligned} \mathcal{L}_t^{-1} \left\{ \frac{1}{(s)^{1/2} + a} \frac{1}{(s)^{1/2} + b} \right\} \\ = \frac{1}{b - a} [b \exp(b^2 t) \operatorname{erfc}(b(t)^{1/2}) \\ - a \exp(a^2 t) \operatorname{erfc}(a(t)^{1/2})] \quad (10) \end{aligned}$$

Case 4 was considered by *Kreft and Zuber [1978]* for flux injection and detection. We also included a resident inlet condition, which may sometimes be evoked for semi-infinite media as well.

Solutions for a Dirac delta application are presented in Appendix B. The four cases involve the instantaneous application of a solute mass m to a porous medium with a cross-sectional area of the liquid phase of $A\theta$, where A is the bulk area and θ the volumetric or areal liquid fraction. Since the Laplace transform of a Dirac delta function is equal to unity, solutions in the Laplace domain can be readily used to obtain expressions for the solute transfer function, which is the ratio of the output and input concentration in the Laplace domain [*Jury and Roth, 1990; Sardin et al., 1991*].

A moving coordinate system was again used for the infinite medium. The solution for the resident injection and detection mode (case 1) is straightforward. The solution for a flux detection mode was obtained by applying transformation (1) to the initial condition of case 1 and using the property $\partial \delta(x)/\partial x = -\delta(x)/x$ [*Roach, 1982*].

Only a flux-type injection was considered by *Kreft and Zuber [1978]* for semi-infinite media; the corresponding auxiliary conditions are shown for cases 3 and 4 in Appendix B. However, a resident mode solute application may be more appropriate for initial value problems; for example, a solute mass m is initially located at the surface, $x = 0$, and subsequently

leached downward with solute-free water. The accompanying conditions are shown for cases 3 and 4, with a respective zero-flux and zero-concentration condition at the inlet.

Solutions for an arbitrary initial condition $f(x)$ or boundary condition $g(t)$ can be readily obtained from the solutions for the Dirac delta function using a Green's function approach. Integration of the results in Appendix B yields the respective expressions

$$C(x, t) = \int_{-\infty}^{\infty} \frac{f(x - \eta)}{(4\pi Dt)^{1/2}} \exp\left[-\frac{(\eta - vt)^2}{4Dt}\right] d\eta \quad (11)$$

$$C(x, t) = \int_{-\infty}^{\infty} \frac{f(x - \eta)}{(4\pi Dt)^{1/2}} \exp\left[-\frac{(\eta - vt)^2}{4Dt}\right] \cdot \left(1 + \frac{D}{v(x - \eta)}\right) d\eta \quad (12)$$

$$C(x, t) = \int_0^t vg(t - \tau) \left\{ \frac{1}{(\pi D \tau)^{1/2}} \exp\left[-\frac{(x - v\tau)^2}{4D\tau}\right] - \frac{v}{2D} \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x + v\tau}{(4D\tau)^{1/2}}\right) \right\} d\tau \quad (13)$$

$$C(x, t) = \int_0^t \frac{xg(t - \tau)}{(4\pi D\tau^3)^{1/2}} \exp\left[-\frac{(x - v\tau)^2}{4D\tau}\right] d\tau \quad (14)$$

Solutions for a combined initial and boundary value problem are obtained by summing up the individual solutions according to the superposition principle.

Time- and Length-Averaged Concentrations

Time- and length-averaged concentrations can be obtained by substituting the macroscopic concentrations into (2) and (3), respectively. The alternative of applying the time- or length-averaged operator to the entire mathematical problem, as is customarily done to transform the intractable microscopic problem to a more manageable macroscopic problem, and the subsequent solution of the discrete concentration does not appear convenient, as was explained in the introduction. Expressions for C_T and C_L can be readily derived for the cases presented in Appendices A and B using the Laplace transform with respect to time. Time-averaged concentrations were obtained according to [Spiegel, 1991]

$$C_T(x, t_2; \Delta t) = \frac{1}{\Delta t} \mathcal{L}_t^{-1} \left\{ \frac{1}{s} \bar{C}(x, s) \right\} \Big|_{t_1}^{t_2} \quad (15)$$

The length-averaged solution was derived by carrying out the integration with respect to distance in the temporal Laplace domain followed by inversion to give

$$C_L(x_2, t; \Delta x) = \frac{1}{\Delta x} \mathcal{L}_t^{-1} \left\{ \int_{x_1}^{x_2} \bar{C}(x, s) dx \right\} \quad (16)$$

The procedure of using results in the Laplace domain may be particularly beneficial for more complicated (linear) transport problems than the one given by (4).

Appendices C and D list the time- and length-averaged concentrations for a Heaviside (compare Appendix A) and a

Dirac application (compare Appendix B), respectively. The solutions were obtained with the table of Laplace transforms given by *van Genuchten and Alves* [1982].

The solutions in Appendices C and D provide an exact description for the (discrete) time- and length-averaged concentrations as a result of continuous or instantaneous solute application. Commonly, the continuous solutions are shifted along the t or x coordinate axes to analyze experimental concentration profiles according to

$$C_{ST}(x, t) = C(x, t_2 - k\Delta t)$$

$$C_{SL}(x, t) = C(x_2 - k\Delta x, t) \quad (0 \leq k \leq 1) \quad (17)$$

where the subscripts ST and SL denote a shift in time or length, respectively. Typically, $k = 1/2$; the effluent concentration at the final time t_2 is then described with the continuous solution using the arithmetic mean of the initial and final sampling times as independent variable. Similarly, the concentration obtained from a core sample is described with the concentration using the centroid of the core as independent variable.

A discrete spatial and temporal moment analysis was conducted to quantify differences between the averaged and shifted concentration profiles for a Dirac distribution. Values for the "moments" of the averaged and shifted profiles were determined numerically from the theoretical concentrations at the end of each sampling interval, assuming the same model parameters. Temporal and spatial moments of the averaged and shifted points were calculated using the trapezoidal rule; for a constant sampling interval this leads to

$$m_p^T(x) = \sum_{i=1}^n t_i^p C_T(x, t_i) \Delta t \quad (18a)$$

$$m_p^S(x) = \sum_{i=1}^n t_i^p C_{ST}(x, t_i - k\Delta t) \Delta t \quad (18b)$$

$$m_p^L(t) = \sum_{i=1}^n x_i^p C_L(x_i, t) \Delta x \quad (19a)$$

$$m_p^S(t) = \sum_{i=1}^n x_i^p C_{SL}(x_i - k\Delta x, t) \Delta x \quad (19b)$$

where p is the order of the moment (0, 1, or 2), n is the number of sampling points, and $m_p^S(x)$ and $m_p^S(t)$ denote discrete moments for concentration data shifted versus time and position, respectively.

The moments were normalized by dividing the numerical results according to (18) and (19) by the zeroth moment. The zeroth moment was derived from the solutions in Appendix B in a similar manner as C_T and C_L according to (15) and (16). Expressions for $m_0(x)$, which is always equal to $m/\theta A v$, and $m_0(t)$ are included in Appendix B. Normalized moments M_p can be defined by dividing the regular moments with the corresponding zeroth moment, i.e., $M_p = m_p/m_0$.

The approximate amount of solute, as predicted by the solutions for the shifted or averaged concentrations, relative to the actual amount of solute that was initially applied or present in the column, percentage of mass recovery, is given by M_0 . The mean of the solute profile, that is, the mean breakthrough time for a temporal distribution or the mean depth for a spatial

Table 1. Moments for Shifted and Time-Averaged Breakthrough Curves as a Result of a Dirac Delta Application

| Moment | Concentration Type* | | | | | | |
|---------|---------------------|-----------|--------|----------|--------|----------|--------|
| | At = 0 | At = 0.01 | | At = 0.1 | | At = 0.2 | |
| | | T | S | T | S | T | S |
| Case 1 | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 |
| M_1 | 1.020 | 1.025 | 1.025 | 1.075 | 1.075 | 1.120 | 1.121 |
| μ_2 | 0.0208 | 0.0208 | 0.0208 | 0.0218 | 0.0208 | 0.0241 | 0.0191 |
| Case 2 | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 |
| M_1 | 1.010 | 1.015 | 1.015 | 1.065 | 1.065 | 1.110 | 1.111 |
| μ_2 | 0.0205 | 0.0205 | 0.0205 | 0.0215 | 0.0205 | 0.0238 | 0.0188 |
| Case 3 | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 |
| M_1 | 1.010 | 1.015 | 1.015 | 1.065 | 1.065 | 1.110 | 1.111 |
| μ_2 | 0.0203 | 0.0203 | 0.0203 | 0.0213 | 0.0203 | 0.0236 | 0.0185 |
| Case 4 | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 |
| M_1 | 1.000 | 1.005 | 1.005 | 1.055 | 1.055 | 1.100 | 1.101 |
| μ_2 | 0.0200 | 0.0200 | 0.0200 | 0.0210 | 0.0200 | 0.0233 | 0.0182 |

Values are $m = 100$, $A = 25$, $v = 10$, $D = 1$, $\theta = 0.5$, $m_0 = 0.8$, and $x = 10$.
 *Time moments are based on time-averaged (T), shifted (S, $k = 1/2$), or continuous (At = 0) concentrations.

distribution, follows from M_1 . The second central moment or variance is given according to

$$\mu_2 = M_2 - M_1^2 \tag{20}$$

where M_1 and M_2 can be any type of normalized moment (i.e., shifted or averaged, spatial or temporal). The variance quantifies solute spreading around the mean of the profile. Experimental values for M_1 and M_2 can be used, for instance, to determine v and D [cf. *Leij and Dane, 1992*].

The practice of shifting the analytical solution for describing discrete values from core or effluent samples to estimate D was evaluated using the relative expressions

$$\frac{\Delta \mu_2(x)}{\mu_2(x)} = \frac{|\mu_2^T(x) - \mu_2^S(x)|}{\mu_2^T(x)} \tag{21a}$$

$$\frac{\Delta \mu_2(t)}{\mu_2(t)} = \frac{|\mu_2^L(t) - \mu_2^S(t)|}{\mu_2^L(t)} \tag{21b}$$

These expressions are based on the notion that μ_2^T and μ_2^L are the appropriate expressions for describing time- and length-averaged concentrations, respectively, while μ_2^S denotes the variance of the concentration profile shifted versus time or distance.

Applications

The first part of this section contains numerical results for spatial and temporal moments as a function of the sampling interval following instantaneous solute application for the four cases in Appendix B using several values for v and D . The last part of the section includes graphical results involving (1) the relative difference in μ_2 for different sampling times and lengths, (2) the concentration versus time for step displacement using time averaging and two types of shifting ($k = 0$ or OS), and (3) the use of length-averaged concentrations for

diffusion experiments ($v = 0$). Note that no units are provided for the parameters in these hypothetical examples; any consistent set can be used (e.g., centimeters for x and days for t).

Table 1 contains values for the temporal moments M_0 , M_1 , and μ_2 for different sampling times At and a relatively small dispersivity ($D/v = 0.1$). The moments are calculated from time-averaged (T) and shifted (S) concentrations. Continuous moments ($At \rightarrow 0$) were calculated using the expressions by *Kreft and Zuber [1978]*. Although there are some quantitative differences between the four solutions, moments predicted according to each solution show a similar behavior for different sample times. The value for M_0 is always equal to unity for time-averaged (T) moments while M_0 for shifted (S) moments starts fluctuating slightly at $At = 0.2$. Values for M_1 are quite similar for the time-averaged and shifted concentrations. The value of M_1 tends to increase with the sampling time period (about 10% when $At = 0.2$). Differences in μ_2 are slightly more pronounced; μ_2 increases slightly but steadily for time-averaged concentrations, whereas it is more variable for shifted concentrations.

Table 2 shows results for the zeroth-, first-, and second-order spatial moments for case 3 in Appendix B, that is, instantaneous solute application at $t = 0$ with observations in the resident mode. The moments, shown for four sampling lengths Ax , were calculated from length-averaged and shifted concentrations using four combinations of v , D , and t (i.e., the time between solute application and sampling). If length-averaged concentrations are used, M_0 equals unity except for the last case ($vt/L = 0.5$ and $D = 100$), where part of the solute has already moved beyond $x = L$ (the maximum depth for the moment calculation). The values for the shifted moments tend increasingly to deviate from the length-averaged moments, where Ax increases, particularly for smaller D . The shifted points, as predicted by the continuous solution, may not be representative for the observations; a few poorly positioned

Table 2. Moments for Shifted and Length-Averaged Breakthrough Curves as a Result of Dirac Delta Application for Flux Injection (FI) and Resident Detection (RD)

| Moment | Concentration Type* | | | | | | | |
|------------------|---------------------|--------|----------------|--------|-----------|--------|-----------|--------|
| | $\Delta x = 1$ | | $\Delta x = 5$ | | $Ax = 10$ | | $Ax = 20$ | |
| | L | S | L | S | L | S | L | S |
| $t = 1, D = 1$ | | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 0.585 | 1.000 | 0.010 | 1.000 | 5.670 |
| M_1 | 10.60 | 10.60 | 12.64 | 7.50 | 15.28 | 0.17 | 20.00 | 113.39 |
| M_2 | 114.4 | 114.3 | 166.0 | 99.7 | 258.4 | 3.0 | 400.0 | 2267.9 |
| $t = 1, D = 100$ | | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 1.002 | 1.000 | 1.009 | 1.000 | 1.031 |
| M_1 | 20.50 | 17.70 | 19.74 | 19.73 | 22.37 | 22.33 | 27.87 | 27.91 |
| M_2 | 542.7 | 425.4 | 502.4 | 500.2 | 614.7 | 605.7 | 895.1 | 857.5 |
| $t = 5, D = 1$ | | | | | | | | |
| M_0 | 1.000 | 1.000 | 1.000 | 0.999 | 1.000 | 0.722 | 1.000 | 2.526 |
| M_1 | 50.60 | 50.60 | 52.60 | 52.56 | 55.13 | 39.88 | 60.00 | 151.54 |
| M_2 | 2570.4 | 2570.3 | 2778.8 | 2774.9 | 3064.4 | 2221.5 | 3601.0 | 9092.3 |
| $t = 5, D = 100$ | | | | | | | | |
| M_0 | 0.920 | 0.920 | 0.920 | 0.920 | 0.920 | 0.921 | 0.920 | 0.926 |
| M_1 | 50.98 | 50.97 | 52.81 | 52.83 | 55.09 | 55.20 | 59.60 | 60.11 |
| M_2 | 3321.5 | 3321.0 | 3528.9 | 3530.0 | 3798.1 | 3804.9 | 4368.5 | 4402.7 |

Values are $m = 50$, $A = 10$, $\theta = 0.5$, $v = 10$, and $L = 100$.
 *Solute concentration according to length-averaged (L) expression in Appendix D or shifted (S) expression in Appendix B.

sampling depths may lead to large differences between the shifted and actual concentration values. The differences in “length-averaged” and “shifted” values of either M_1 or M_2 show a similar behavior as for M_0 with increased deviations for smaller D and greater Ax .

The bias in D as a result of shifting the solution of the ADE can be illustrated by plotting the relative difference in μ_2 , as given by (21), versus $v\Delta t$ or Ax . Figure 2 shows $\Delta\mu_2(x)/\mu_2(x)$ as a function of $v\Delta t$ for instantaneous solute application to a semi-infinite column with both application (at $x = 0$) and detection (at $x = 10$) in the flux mode (case 4 in Appendix B). A value of $v\Delta t = 1$ cm in this example would amount to an effluent volume of 12.5 cm³. The solid line is for a relatively small dispersivity of 0.1, while the dashed line is for a higher dispersivity of 10. The variations in μ_2 depend on how well the sampling can capture the behavior of the breakthrough curve for a particular sampling schedule at a certain position. The relative error for a dispersivity of 10 is quite low, with a max-

imum relative difference of only 1% at $v\Delta t = 2$, the corresponding error for the lower dispersivity of 0.1 is about 22%, while the error for $v\Delta t = 1$ is 4%. This error will likely increase for more complex solute applications than the Dirac function.

Figure 3 shows similar relationships for the determination of the concentration versus depth, for example, by soil coring. The mathematical conditions for instantaneous solute application are probably best described with case 3 in Appendix B. Figure 3 shows $\Delta\mu_2(t)/\mu_2(t)$ as a function of sample length Ax for two values of vt/L and two values for D . The relative error decreases when the solute peak travels a greater distance in the medium, as expressed by the dimensionless time vt/L and when dispersion increases. For a core length of 6 cm the relative error in μ_2 varies between 0.2 and 8.4% for this example, but considerably greater discrepancies are obtained for larger sampling lengths. If, instead of the centroid of the sample, another position is used as independent variable in the

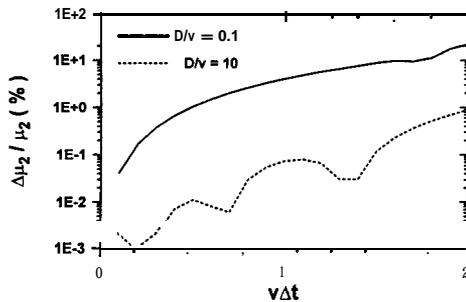


Figure 2 Relative difference in variance ($\Delta\mu_2/\mu_2$) between the time-averaged and shifted concentration ($k = 0.5$) at $x = 10$ for the fourth case of a Dirac injection, as a function of sampling time ($\sim v\Delta t$) using $D/v = 0.1$ or 10 ($\theta = 0.5$, $m = 100$, $A = 25$).

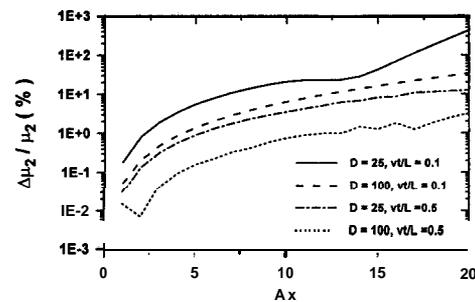


Figure 3 Relative difference in variance ($\Delta\mu_2/\mu_2$) between the length-averaged and shifted concentration ($k = 0.5$) for the third case of a Dirac injection, as a function of sampling length (Ax) using $vt/L = 0.1$ or 0.5 ($v = 10$ and $L = 100$), and $D = 25$ or 100, with $A = 10$ and $\theta = 0.5$.

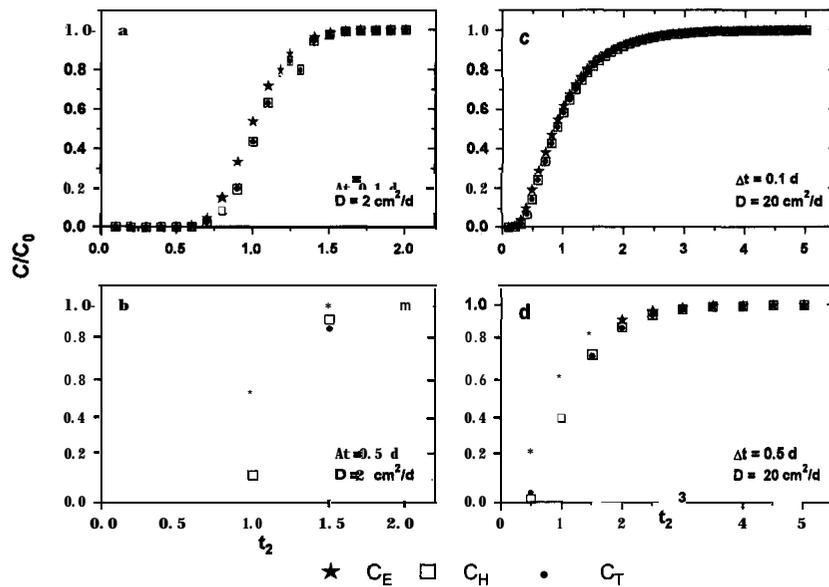


Figure 4. Predicted breakthrough points at $x = 10$ for the fourth case of a Heaviside application using the time-averaged concentration C_T and the continuous solution halfway C_H and at the end C_E of the sampling interval (shifted with $k = 1/2$ and 0 , respectively) with (a) $v = 10$, $D = 2$, and $At = 0.1$; (b) $v = 10$, $D = 2$, and $At = 0.5$; (c) $v = 10$, $D = 20$, and $At = 0.1$; and (d) $v = 10$, $D = 20$, and $At = 0.5$.

continuous expression for the concentration, the error will normally increase.

The role of the invoked mathematical solution to model discrete data points can also be illustrated by comparing time- or length-averaged concentrations obtained with shifted concentration curves. Figure 4 shows breakthrough data for a step input (case 4 in Appendix A), as predicted for two sampling times ($At = 0.1$ or 0.5) and two dispersion coefficients ($D = 2$ or 20) at $x = 10$ with $v = 10$. The effluent data are predicted according to case 4 at the sampling times with the time-averaged concentration in Appendix C, denoted as C_T , and the shifted (continuous) concentration from Appendix A. Results are for the “halfway” solution $C_H = C_{ST}(x, t_2 - 0.5\Delta t)$ and the “end” solution $C_E = C_{ST}(x, t_2)$. While obviously erroneous, the latter practice was included for illustrative purposes following the work by **Schnabel and Richie [1987]**. Figure 4a displays the data for $At = 0.1$; if time is expressed in days, this example corresponds to an effluent volume of 10 cm^3 for $A = 25 \text{ cm}^2$ and $\theta = 0.4 \text{ cm}^2/\text{cm}^2$. The C_H and C_T profiles are virtually identical, while the C_E curve predicts earlier breakthrough. Figure 4b is for a larger sampling time interval $At = 0.5$; the C_H and C_T profiles show a relatively greater difference. The use of C_E is completely inappropriate here for describing effluent data. The closest match between C_T , C_E , and C_H is obtained in Figure 4c for a

relatively small At and a large D (hence a larger time range was selected to plot the results). Even C_E describes the data fairly well. Figure 4d also pertains to a fairly large D but with a larger sampling interval.

The ramifications of using a continuous model in parameter optimization procedures involving discrete data were assessed by describing the time-averaged data from the example illustrated in Figure 4 with the two continuous solutions ($k = 0$ or 0.5). Table 3 shows the fitted values for v and D , as obtained with the program CXTFIT [**Parker and van Genuchten, 1984b**], along with the correct parameter values which also served as initial estimates in the optimization procedure. The difference between fitted and actual parameters was the greatest for C_E (no shifting), with a poorer fit for the larger sampling interval. Notice that the curve fitting, in effect, creates its own shift by consistently underestimating v . Alternatively, the fit could have been improved by including the retardation factor R in the optimization procedure [cf. **Barty, 1988**]. On the other hand, if v was excluded from the optimization because it was obtained independently, the results would have been worse. A considerably better fit was achieved for C_H ; the best fit is again for the smaller sampling time ($At = 0.1$) and the higher dispersion coefficient ($D = 20$).

The use of length averaging is presented in a somewhat different context, namely, for the determination of diffusion

Table 3. Fitting v and D to Discrete Experimental (Time-Averaged) Data From Figure 4 With the Continuous Solutions C_E and C_H

| Case | At | Actual Value | | Fitted With C_E | | Fitted With C_H | |
|-----------|-----|--------------|------|-------------------|-------|-------------------|-------|
| | | v | D | v | D | v | D |
| Figure 4a | 0.1 | 10.0 | 2.00 | 9.524 | 1.761 | 9.996 | 2.042 |
| Figure 4b | 0.5 | 10.0 | 2.00 | 8.016 | 1.633 | 10.029 | 3.260 |
| Figure 4c | 0.1 | 10.0 | 20.0 | 9.559 | 17.02 | 9.995 | 20.04 |
| Figure 4d | 0.5 | 10.0 | 20.0 | 8.051 | 10.34 | 9.872 | 20.73 |

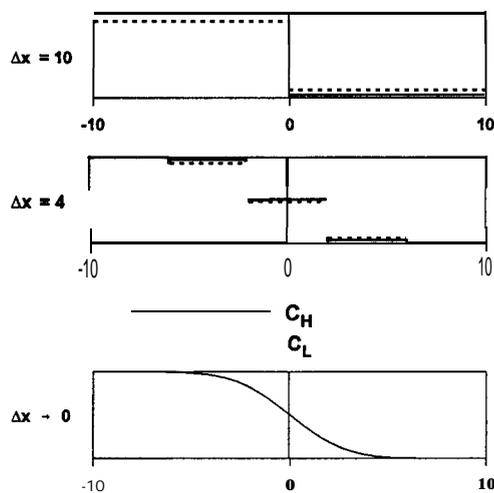


Figure 5. Predicted concentrations as a result of diffusion with $D = 0.5$ at $t = 5$ using the discrete analysis with the length-averaged concentration C_L or the shifted concentration C_H for a sampling interval (top) $\Delta x = 10$ or (middle) $\Delta x = 4$ and (bottom) the continuous analysis with the macroscopic concentration according to case 1 of Appendix A.

coefficients through destructive sampling. This application serves as an example for many cases where the use of explicit expressions for time- or length-averaged concentrations may improve the estimation of model parameters and reduce the time and expenses associated with experimental procedures. A value for D is determined by bringing two columns together at $t = 0$ such that $C = C_0$ for $x < 0$ and $C = 0$ for $x > 0$ at that time; the columns are sectioned after a certain amount of time has elapsed [e.g., Van Rees *et al.*, 1991]. The mathematical solution of the problem is subsequently fitted to the solute concentration of each segment to determine D . This scenario was modeled with a modified solution of case 1 in Appendix A ($v = 0$), assuming a diffusion coefficient $D = 0.5$. Figure 5 shows schematics of the solute profile at $t = 5$. The macroscopic concentration distribution, as predicted with the continuous solution, is shown at the bottom, whereas the top two sketches pertain to the length-averaged (C_L) and shifted (C_H) concentrations. We note again that C_L provides an exact description of the concentration at the centroid of the core, the approximation with C_L can be made quite accurate but at the expense of taking and analyzing more samples. In many cases the value of D is not precisely known a priori, in which case one may be inclined to overestimate the required number of samples. A description with length-averaged concentrations offers flexibility in deciding when to sample and what sample size to use. Of course, a certain minimum number of samples may need to be taken because of limitations in experimental resolution or nonlinear optimization and to check assumptions regarding boundary conditions. The use of time- and length-averaged concentrations may also be fruitful for other transport problems because of added flexibility in the choice of sample size and possibly an improved mathematical analysis of the observations.

Summary and Conclusions

Several averaging procedures were defined for the solute concentration. These procedures arise during the prediction and analysis of experimental solute transport data in porous

media as described with the advection-dispersion equation. Solute concentrations are commonly expressed in terms of resident or flux modes, which are both continuous dependent variables in the ADE. The selection of either a resident or flux-averaged concentration depends on the invoked or assumed solute application and detection modes. The selection, in turn, determines the formulation of the boundary conditions. Analytical solutions, including intermediate solutions in the Laplace or Fourier domain, were given in Appendices A and B using four combinations of detection and injection modes for continuous and instantaneous solute application.

Many experimental studies lead to solute concentrations measured over larger spatial or temporal scales than those for which the ADE is formulated (e.g., soil coring or effluent sampling). These large scales lead to discrete experimental concentration variables that can only be used in an approximate manner as a dependent variable in the continuous ADE. Parameter estimation procedures based on continuous solutions of the ADE will therefore only yield approximate results, and the experimental results are better described using (integral) averaged solutions of the ADE. Expressions for the time- and length-averaged concentrations were presented in Appendices C and D (first objective).

Frequently, an (implicitly) averaged value is used for the independent variable when fitting a continuous solution of the ADE to experimental data. Such an approach amounts to shifting of the ADE. A moment analysis was carried out to compare the use of shifted and (integral) averaged expressions for the concentration to describe experimental data points. Values for moments that characterize mass conservation, advection, and dispersion were derived as a function of sampling time or length using several values for v and D . The time- and length-averaged expressions always conserved mass, whereas the mass balance of the shifted solutions tended to fluctuate at larger sampling intervals because of insufficient sampling points to characterize the spatial or temporal distribution of the solute, especially for low values of D . Higher-order moments displayed this behavior more strongly. The relative error in the second central moment μ_2 , which is indicative of discrepancies in D when a shifted solution of the ADE is used, was plotted as a function of sampling time. The difference in μ_2 was found to be 1% if $v\Delta t/D \approx 0.05$ and $D = 1$, while a 4 times greater sampling time ($v\Delta t/D \approx 0.2$) resulted in a similar error for $D = 100$. A similar analysis was also conducted for length averaging; for a sample length of 5 and $v = 10$ an error of 5% occurred at sampling time $t = 1$ if $D = 25$, while the error was only 0.2% at $t = 5$ when $D = 100$. Errors in μ_2 grew with sampling time or length, while smaller values for D also tended to increase these errors.

Solute concentrations were also predicted at sampling times using the averaged expression for the concentration and using solutions of the ADE halfway (C_L) or at the end (C_H) of the sampling period. The use of C_L generally leads to a poor description of the experimental data, while C_H usually resembles the value according to the (exact) averaged expression. On the basis of graphical and numerical results for solute breakthrough curves, it appears that shifting the concentration profile, that is, as predicted with a continuous model, by half the sampling interval is generally a good approximation for the actual concentration of a sample (second objective).

An advantage of averaged solutions is that they yield an exact description of the data, provided that the transport model is correct, thus requiring fewer samples for parameter

estimations. The increased flexibility in experimentation is especially beneficial if no a priori knowledge is available of the transport parameters. The expressions for the averaged concentrations presented in this paper can be readily implemented; they are only slightly more complicated than traditional continuous solutions of the ADE.

Appendix A: Solutions for Heaviside Application

Case 1

Initial and boundary conditions for infinite medium (RI and RD) are

$$\begin{aligned} C(x, 0) &= C_0H(-x) & -\infty < x < \infty \\ C(-\infty, t) &= C_0 & t > 0 \\ C(+\infty, t) &= 0 & t > 0 \\ H(-x) &= 1 & x < 0 \\ H(-x) &= 1/2 & x = 0 \\ H(-x) &= 0 & x > 0 \end{aligned}$$

Expressions for concentration (*a*, *b*, and *k* are given by (8)) are

$$\begin{aligned} C(x, t) &= \frac{C_0}{2} \operatorname{erfc} \left(\frac{x - vt}{(4Dt)^{1/2}} \right) \\ \bar{C}(x, s) &= \frac{C_0}{2} \exp(ak - k(s + a)^{1/2}) \left(\frac{1}{s} + \frac{a}{s(s + a^2)^{1/2}} \right) \\ \hat{C}(\alpha, t) &= \frac{C_0}{i\alpha(2\pi)^{1/2}} \exp(-\alpha^2Dt) \end{aligned}$$

Case 2

Initial and boundary conditions for infinite medium (RI and FD) are

$$\begin{aligned} C(x, 0) &= C_0H(-x) \left[1 + \frac{2D}{v} \delta(x) \right] & -\infty < x < \infty \\ C(-\infty, t) &= C_0 & t > 0 \\ C(+\infty, t) &= 0 & t > 0 \end{aligned}$$

Expressions for concentration are

$$\begin{aligned} C(x, t) &= \frac{C_0}{2} \left\{ \operatorname{erfc} \left(\frac{x - vt}{(4Dt)^{1/2}} \right) + \left(\frac{D}{\pi v^2 t} \right)^{1/2} \exp \left[-\frac{(x - vt)^2}{4Dt} \right] \right\} \\ \bar{C}(x, s) &= \frac{C_0}{2} \exp(ak - k(s + a^2)^{1/2}) \cdot \left[\frac{1}{s} + \frac{a}{s(s + a^2)^{1/2}} + \frac{1}{2a(s + a^2)^{1/2}} \right] \\ \hat{C}(\alpha, t) &= \frac{C_0}{(2\pi)^{1/2}} \left(\frac{1}{i\alpha} + \frac{D}{v} \right) \exp(-\alpha^2Dt) \end{aligned}$$

Case 3

Initial and boundary conditions for semi-infinite medium (FI and RD) are

$$\begin{aligned} C(x, 0) &= 0 & 0 < x < \infty \\ \left(C - \frac{D}{v} \frac{\partial C}{\partial x} \right) \Big|_{x=0^+} &= C_0H(t) & t > 0 \\ C(+\infty, t) &= 0 & t > 0 \end{aligned}$$

Expressions for concentration are

$$\begin{aligned} C(x, t) &= \frac{C_0}{2} \left\{ \operatorname{erfc} \left(\frac{x - vt}{(4Dt)^{1/2}} \right) + \left(\frac{4v^2t}{\pi D} \right)^{1/2} \exp \left[-\frac{(x - vt)^2}{4Dt} \right] - \left(1 + \frac{vx}{D} + \frac{v^2t}{D} \right) \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x + vt}{(4Dt)^{1/2}} \right) \right\} \\ \bar{C}(x, s) &= \frac{2a}{a + (s + a^2)^{1/2}} \frac{C_0}{s} \exp(ak - k(s + a^2)^{1/2}) \\ \bar{C}(p, t) &= \frac{vC_0}{b - a} \left\{ \frac{b}{b^2 - a^2} \exp[(b^2 - a^2)t] \operatorname{erfc}(b(t)^{1/2}) + \frac{b^2 + a^2}{2a(b^2 - a^2)} \operatorname{erf}(a(t)^{1/2}) - \frac{b}{b^2 - a^2} - at \operatorname{erfc}(a(t)^{1/2}) + (t/\pi)^{1/2} \right\} \end{aligned}$$

Case 4

Initial and boundary conditions for semi-infinite medium (FI and FD, RI and RD, RI and FD) are

$$\begin{aligned} C(x, 0) &= 0 & 0 < x < \infty \\ C(0, t) &= C_0H(t) & t > 0 \\ C(+\infty, t) &= 0 & t > 0 \end{aligned}$$

Expressions for concentration are

$$\begin{aligned} C(x, t) &= \frac{C_0}{2} \left\{ \operatorname{erfc} \left(\frac{x - vt}{(4Dt)^{1/2}} \right) + \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x + vt}{(4Dt)^{1/2}} \right) \right\} \\ \bar{C}(x, s) &= \frac{C_0}{s} \exp(ak - k(s + a^2)^{1/2}) \\ \bar{C}(p, t) &= \frac{vC_0}{a^2 - b^2} \{ 2[a \operatorname{erf}(a(t)^{1/2}) - b] + b \exp(b^2t) \operatorname{erf}(b(t)^{1/2}) \} \end{aligned}$$

Appendix B: Solutions for Dirac Application

Case 1

Mathematical conditions and $m_0(t)(m_0(x) = m/\theta Av)$ for infinite medium (RI and RD) are

$$\begin{aligned} C(x, 0) &= \frac{m}{\theta A} \delta(x) & -\infty < x < \infty \\ C(-\infty, t) &= 0 & t > 0 \end{aligned}$$

$$C(+\infty, t) = 0 \quad t > 0$$

$$m_0(t) = \frac{m}{2\theta A} \operatorname{erfc} \left(-\left(\frac{v^2 t}{4D}\right)^{1/2} \right)$$

Expressions for concentration are

$$C(x, t) = \frac{m}{\theta A (4\pi Dt)^{1/2}} \exp \left[-\frac{(x - vt)^2}{4Dt} \right]$$

$$\bar{C}(x, s) = \frac{m}{2\theta A (D)^{1/2}} \frac{\exp(ak - k(s + a^2)^{1/2})}{(s + a^2)^{1/2}}$$

$$\hat{C}(\alpha, t) = \frac{m}{\theta A (2\pi)^{1/2}} \exp(-\alpha^2 Dt)$$

Case 2

Mathematical conditions and $m_0(t)(m_0(x) = m/\theta A v)$ for infinite medium (RI and FD) are

$$C(x, 0) = \frac{m}{\theta A} \left(1 + \frac{D}{vx} \right) \delta(x) \quad -\infty < x < \infty$$

$$C(-\infty, t) = 0 \quad t > 0$$

$$C(+\infty, t) = 0 \quad t > 0$$

$$m_0(t) = \frac{m}{2\theta A} \left[\left(\frac{D}{\pi v^2 t} \right)^{1/2} \exp \left(-\frac{v^2 t}{4D} \right) + \operatorname{erfc} \left(-\left(\frac{v^2 t}{4D}\right)^{1/2} \right) \right]$$

Expressions for concentration are

$$C(x, t) = \frac{m}{2\theta A v (4\pi Dt^3)^{1/2}} \exp \left[-\frac{(x - vt)^2}{4Dt} \right]$$

$$\bar{C}(x, s) = \frac{m}{2\theta A v} \exp(ak - k(s + a^2)^{1/2}) \left[1 + \frac{a}{(s + a^2)^{1/2}} \right]$$

$$\hat{C}(\alpha, t) = \frac{m}{\theta A (2\pi)^{1/2}} \left(1 + \frac{i\alpha D}{v} \right) \exp(-\alpha^2 Dt)$$

Case 3

Mathematical conditions and $m_0(t)(m_0(x) = m/\theta A v)$ for semi-infinite medium (FI and RD) are

$$C(x, 0) = 0 \quad 0 < x < \infty$$

$$\left(C - \frac{D}{v} \frac{\partial C}{\partial x} \right) \Big|_{x=0^+} = \frac{m}{\theta A v} \delta(t) \quad t > 0$$

$$C(+\infty, t) = 0 \quad t > 0$$

(RI and RD)

$$C(x, 0^+) = \frac{m}{\theta A} \delta(x) \quad 0^- \leq x < \infty$$

$$\left(C - \frac{D}{v} \frac{\partial C}{\partial x} \right) \Big|_{x=0^+} = 0 \quad t > 0$$

$$C(+\infty, t) = 0 \quad t > 0$$

$$m_0(t) = m/\theta A$$

Expressions for concentration are

$$C(x, t) = \frac{m}{\theta A} \left\{ \frac{1}{(\pi Dt)^{1/2}} \exp \left[-\frac{(x - vt)^2}{4Dt} \right] \right.$$

$$\left. - \frac{v}{2D} \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x + vt}{(4Dt)^{1/2}} \right) \right\}$$

$$\bar{C}(x, s) = \frac{m}{\theta A v a + (s + a^2)^{1/2}} \exp(ak - k(s + a^2)^{1/2})$$

$$\bar{C}(p, t) = \frac{m}{\theta A} \frac{1}{p(D)^{1/2} - 2a}$$

$$\cdot \{(p(D)^{1/2} - a) \operatorname{erfc} [(p(D)^{1/2} - a)t]$$

$$\cdot \exp [(p(D)^{1/2} - 2a)p(Dt)^{1/2}] - a \operatorname{erfc} (a(t)^{1/2})\}$$

Case 4

Mathematical conditions and $m_0(t)(m_0(x) = m/\theta A v)$ for semi-infinite medium (FI and FD) are

$$C(x, 0) = 0 \quad 0 < x < \infty$$

$$C(0, t) = \frac{m}{\theta A v} \delta(t) \quad t > 0$$

$$C(+\infty, t) = 0 \quad t > 0$$

(RI and FD)

$$C(x, 0^+) = \frac{m}{\theta A} \left(1 + \frac{D}{vx} \right) \delta(x) \quad 0^- < x < \infty$$

$$C(0, t) = 0 \quad t > 0$$

$$C(+\infty, t) = 0 \quad t > 0$$

$$m_0(t) = \frac{m}{2\theta A} \left[\left(\frac{4D}{\pi v^2 t} \right)^{1/2} \exp \left(-\frac{v^2 t}{4D} \right) + \operatorname{erfc} \left(-\left(\frac{v^2 t}{4D}\right)^{1/2} \right) \right]$$

Expressions for concentration are

$$C(x, t) = \frac{m}{\theta A v (4\pi Dt^3)^{1/2}} \exp \left[-\frac{(x - vt)^2}{4Dt} \right]$$

$$\bar{C}(x, s) = \frac{m}{\theta A v} \exp(ak - k(s + a^2)^{1/2})$$

$$\bar{C}(p, t) = \frac{m}{\theta A} \frac{1}{2a} \left\{ \frac{\exp(-a^2 t)}{(\pi t)^{1/2}} - (p(D)^{1/2} - a) \right.$$

$$\left. \cdot \exp [(p(D)^{1/2} - 2a)p(D)^{1/2} t] \operatorname{erfc} [(p(D)^{1/2} - a)t] \right\}$$

Appendix C: Time- and Length-Averaged Concentrations for Heaviside Application

Case 1

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{C_0}{2\Delta t} \left\{ \left(t - \frac{x}{v} - \frac{D}{v^2} \right) \operatorname{erfc} \left(\frac{x - vt}{(4Dt)^{1/2}} \right) \right.$$

$$\left. + \left(\frac{4Dt}{\pi v^2} \right)^{1/2} \exp \left[-\frac{(x - vt)^2}{4Dt} \right] \right\}$$

$$+ \frac{D}{v^2} \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = \frac{C_0}{2\Delta x} \left\{ (x-vt) \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) - \left(\frac{4Dt}{\pi}\right)^{1/2} \exp\left[-\frac{(x-vt)^2}{4Dt}\right] \right\} \Big|_{x=x_1}^{x=x_2}$$

Case 2

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{C_0}{2\Delta t} \left\{ \left(t - \frac{x}{v}\right) \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) + \left(\frac{4Dt}{\pi v^2}\right)^{1/2} \exp\left[-\frac{(x-vt)^2}{4Dt}\right] \right\} \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = \frac{C_0}{2\Delta x} \left\{ \left(x - vt - \frac{D}{v}\right) \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) - \left(\frac{4Dt}{\pi}\right)^{1/2} \exp\left[-\frac{(x-vt)^2}{4Dt}\right] \right\} \Big|_{x=x_1}^{x=x_2}$$

Case 3

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{C_0}{2\Delta t} \left\{ \left(t - \frac{x}{v} - \frac{D}{v^2}\right) \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) + \left(\frac{4Dt}{\pi v^2}\right)^{1/2} \left(1 + \frac{vx}{2D} + \frac{v^2 t}{2D}\right) \exp\left[-\frac{(x-vt)^2}{4Dt}\right] + \left[\frac{D}{v^2} - t - \frac{(x+vt)^2}{2D}\right] \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = \frac{C_0}{2\Delta x} \left\{ (x-vt) \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) - (x+vt) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{x=x_1}^{x=x_2}$$

Case 4

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{C_0}{2\Delta t} \left\{ \left(t - \frac{x}{v}\right) \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) + \left(t + \frac{x}{v}\right) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = \frac{C_0}{2\Delta x} \left\{ \left(x - vt/R - \frac{D}{v}\right) \operatorname{erfc}\left(\frac{Rx-vt}{(4DRt)^{1/2}}\right) - \left(\frac{4Dt}{\pi R}\right)^{1/2} \exp\left[-\frac{(Rx-vt)^2}{4DRt}\right] + \frac{D}{v} \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{Rx+vt}{(4DRt)^{1/2}}\right) \right\} \Big|_{x=x_1}^{x=x_2}$$

Appendix D: Time- and Length-Averaged Concentrations for Dirac Application**Case 1**

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{1}{2\Delta t} \frac{m}{\theta A v} \left\{ \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) - \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = -\frac{1}{2\Delta x} \frac{m}{\theta A} \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) \Big|_{x=x_1}^{x=x_2}$$

Case 2

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{1}{2\Delta t} \frac{m}{\theta A v} \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = -\frac{1}{2\Delta x} \frac{m}{\theta A} \left\{ \left(\frac{D}{\pi v^2 t}\right)^{1/2} \exp\left[-\frac{(x-vt)^2}{4Dt}\right] + \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{x=x_1}^{x=x_2}$$

Case 3

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{1}{2\Delta t} \frac{m}{\theta A v} \left\{ \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) + \left(\frac{4v^2 t}{\pi D}\right)^{1/2} \exp\left[-\frac{(x-vt)^2}{4Dt}\right] - \left(1 + \frac{vx}{D} + \frac{v^2 t}{D}\right) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = -\frac{1}{2\Delta x} \frac{m}{\theta A} \left\{ \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) + \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{x=x_1}^{x=x_2}$$

Case 4

Expressions for concentration are

$$C_T(x, t_2; \Delta t) = \frac{1}{2\Delta t} \frac{m}{\theta A v} \left\{ \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) + \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left(\frac{x+vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{t=t_1}^{t=t_2}$$

$$C_L(x_2, t; \Delta x) = -\frac{1}{2\Delta x} \frac{m}{\theta A} \left\{ \left(\frac{4D}{\pi v^2 t}\right)^{1/2} \exp\left[-\frac{(x-vt)^2}{4Dt}\right] + \operatorname{erfc}\left(\frac{x-vt}{(4Dt)^{1/2}}\right) \right\} \Big|_{x=x_1}^{x=x_2}$$

References

Barry, D. A., On "Elimination of time assignment bias in estimates of dispersion coefficient," *Soil Sci. Soc. Am. J.*, 52, 896-897, 1988.

- Bear, J., and A. Verruijt, **Modelling Groundwater Flow and Pollution**, 414 pp., D. Reidel, Norwell, Mass., 1987.
- Cushman, J. H., On measurement, scale, and scaling, **Water Resour. Res.**, **22**, 129-134, 1986.
- Dagan, G., **Flow and Transport in Porous Formations**, 465 pp., Springer-Verlag, New York, 1989.
- Fischer, H. B., E. J. List, R. C. Y. Koh, J. Imberger, and N. H. Brooks, **Mixing in Inland and Coastal Waters**, 483 pp., Academic, San Diego, Calif., 1979.
- Hassanizadeh, M., and W. G. Gray, General conservation equations for multi-phase systems, 1, Averaging procedure, Adv. **Water Resour.**, **2**, 131-144, 1979.
- Jury, W. A., and K. Roth, **Transfer Functions and Solute Movement Through Soil: Theory and Applications**, 226 pp., Birkhauser, Basel, Switzerland, 1990.
- Kreft, A., and A. Zuber, On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions, **Chem. Eng. Sci.**, **33**, 1471-1480, 1978.
- Kreft, A., and A. Zuber, Comments on "Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport" by J. C. Parker and M. T. van Genuchten, **Water Resour. Res.**, **22**, 1157-1158, 1986.
- Leij, F. J., and J. H. Dane, Moment method applied to solute transport with binary and ternary exchange, **Soil Sci. Soc. Am. J.**, **56**, 667-674, 1992.
- Parker, J. C., and M. T. van Genuchten, Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport, **Water Resour. Res.**, **20**, 866-872, 1984a.
- Parker, J. C., and M. T. van Genuchten, Determining transport parameters from laboratory and field tracer experiments, **Bull.** **84-3,96** pp., Va. Agric. Exp. Stn., Blacksburg, Va., 1984b.
- Plumb, O. A., and S. Whitaker, Dispersion in heterogeneous porous media, 1, Local volume averaging and large-scale averaging, **Water Resour. Res.**, **24**, 913-926, 1988.
- Roach, G. F., **Green's Functions**, 325 pp., Cambridge University Press, New York, 1982.
- Sardin, M., D. Schweich, F. J. Leij, and M. T. van Genuchten, Modeling the nonequilibrium transport of linearly interacting solutes in porous media: A review, **Water Resour. Res.**, **27**, 2287-2307, 1991.
- Schnabel, R. R., and E. B. Richie, Elimination of time assignment bias in estimates of dispersion coefficient, **Soil Sci. Soc. Am. J.**, **51**, 302-304, 1987.
- Spiegel, M. R., **Laplace Transforms**, 261 pp., McGraw-Hill, New York, 1991.
- Taylor, G. I., Dispersion of soluble matter in solvent flowing slowly through a tube, **Proc. R. Soc. London A**, **219**, 186-203, 1953.
- Toride, N., F. J. Leij, and M. T. van Genuchten, Flux-averaged concentrations for transport in soils having nonuniform initial solute distributions, **Soil Sci. Soc. Am. J.**, **57**, 1406-1409, 1993.
- van Genuchten, M. T., and W. J. Alves, Analytical solutions of the one-dimensional convective-dispersive solute transport equation, **Tech. Bull., U.S. Dep. Agric.** **1661**, 151 pp., 1982.
- van Genuchten, M. T., and J. C. Parker, Boundary conditions for displacement experiments through short laboratory soil columns, **Soil Sci. Soc. Am. J.**, **48**, 703-708, 1984.
- van Genuchten, M. T., and P. J. Wierenga, Solute dispersion coefficients and retardation factors, in **Methods of Soil Analysis**, vol. 1, edited by A. Klute, pp. 1025-1054, American Society of Agronomy, Madison, Wisc., 1986.
- Van Rees, K. C. J., E. A. Sudicky, P. S. C. Rao, and K. R. Reddy, Evaluation of laboratory techniques for measuring diffusion coefficients in sediments, **Environ. Sci. Technol.**, **25**, 1605-1611, 1991.

F. J. Leij and N. Toride, U.S. Salinity Laboratory, 450 Big Springs Road, Riverside, CA 92507.

(Received July 5, 1994; revised February 13, 1995; accepted February 14, 1995.)