DIVISION S-1—SOIL PHYSICS

Flux-Averaged Concentrations for Transport in Soils Having Nonuniform Initial Solute Distributions

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ABSTRACT

The need to distinguish between volume-averaged or resident concentrations (c_r) and flux-averaged or flowing concentrations (c_f) is now widely accepted. Flux-averaged concentrations associated with the convection–dispersion equation (CDE) have been mostly used for solute transport problems involving uniform initial distributions. We present flux-averaged concentrations for nonuniform initial distributions using analytical solution methods for a semi-infinite soil system and numerical methods for a finite system. Mathematically, c_f is equivalent to c_r associated with a first-type inlet condition (rather than a third-type condition) only for semi-infinite soil profiles having uniform initial conditions. We show that, for a stepwise initial distribution, c_f can be both negative or much greater than the initial concentration of c_r, especially during the early stages of solute displacement. This physically odd situation results from the fact that c_f represents a solute flux rather than a directly measurable volumetric concentration. Flux-averaged concentrations at the exit of a finite soil column with a uniform initial distribution are nearly identical to c_f for a semi-infinite system when the column Peclet number is greater than ≈5. However, if the initial distribution involves a high gradient in c_r near the exit, c_f values for finite and semi-infinite systems at the exit can be very different, similarly as those for c_r, because of the adoption of different outlet conditions.

THE CONVECTION–DISPERSION EQUATION has long been used to predict solute transport in soils. Concentration distributions obtained with the CDE depend greatly on the formulation of the boundary and initial conditions. Considerable attention has therefore been paid to the proper formulation of boundary conditions and the description of solute injection and detection modes (Danckwerts, 1953; Wehner and Wilhelm, 1956). The need to distinguish between c_r and c_f has now been widely recognized (Kreft and Zuber, 1978; Parker and van Genuchten, 1984; Jury and Roth, 1990).

The resident concentration is defined as the mass of solute per unit volume of soil solution; this definition is the conventional interpretation of a concentration. Solute transport problems involving c_r are usually solved for third- or flux-type inlet conditions since such conditions ensure that mass balance requirements are satisfied (van Genuchten and Parker, 1984). On the other hand, the flux-averaged concentration is defined as the ratio of the solute mass and water flux densities (Kreft and Zuber, 1978). If solute concentrations are obtained from effluent curves, which are encountered in column displacement experiments, the use of c_f is generally preferable. The use of c_f is also convenient in stochastic models of field-scale solute transport where area-averaged solute fluxes are usually of primary concern (Dagan et al., 1992; Destouni and Cvetkovic, 1991; Jury and Roth, 1990).

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Received 30 Nov. 1992.

Published in Soil Sci. Soc. Am. J. 57:1406–1409 (1993).

Flux-averaged concentrations have been used mostly for solute applications to a soil with a uniform initial distribution (Kreft and Zuber, 1978). For a semi-infinite system, c_f is then mathematically equivalent to c_r if a first- or concentration-type rather than a third-type inlet condition is used. Van Genuchten and Parker (1984) showed that c_f for semi-infinite and finite systems are nearly identical at the exit for column Peclet numbers greater than ≈5.

Although nonuniform initial solute distributions are quite common, relatively little attention has been paid to c_f for such conditions. Our objective was to further investigate c_f for soils having a nonuniform initial solute distribution. Typical examples of c_f for a stepwise initial distribution in semi-infinite and finite systems will be presented.

MATHEMATICAL PROBLEM

One-dimensional solute transport in a homogeneous soil during steady-state flow is generally described with the CDE:

$$R\frac{\partial c_r}{\partial t} = D\frac{\partial^2 c_r}{\partial x^2} - v\frac{\partial c_r}{\partial x} \qquad [1]$$

where R is the retardation factor, c_r is the volume-averaged or resident concentration (M L^{-3}), D is the dispersion coefficient (L^2 T^{-1}), v is the pore-water velocity (L T^{-1}), x is distance (L), and t is time (T).

The initial and boundary conditions for finite and semi-infinite systems are

$$c_r(x,0) = f(x) \qquad [2]$$

$$vc_r(0,t) - D\frac{\partial c_r(0,t)}{\partial x} = vg(t) \qquad [3]$$

$$\frac{\partial c_r}{\partial x}(\ell,t) = 0 \qquad [4a]$$

$$\frac{\partial c_r}{\partial x}(\infty,t) = 0 \qquad [4b]$$

where $f(x)$ is the initial concentration, $g(t)$ is the input concentration, ℓ is outlet of the soil system under consideration, and Eq. [4a] and [4b] give the outlet condition for finite and semi-infinite systems, respectively. Although no "correct" outlet condition can probably be formulated for finite systems (Parlange et al., 1992), a zero concentration gradient (Eq. [4a]) is often used based on the assumption that c_r is macroscopically continuous at the outlet and that no dispersion occurs outside the soil (Danckwerts, 1953; Wehner and Wilhelm, 1956). Solutions for semi-infinite systems may also be applied to finite systems if the assumption is made that solute concentrations upstream of the boundary are not affected by the boundary itself.

The flux-averaged concentration, c_f, is defined as (Kreft and Zuber, 1978)

$$c_f = \frac{J}{q} = c_r - \frac{D}{v}\frac{\partial c_r}{\partial x} \qquad [5]$$

where J (M L^{-2} T^{-1}) and q (L^3 L^{-2} T^{-1}) are the solute and water flux densities, respectively. Application of the above transformation to Eq. [1] through [4] yields the following transport problem in terms of c_f (Parker and van Genuchten, 1984):

$$R\frac{\partial c_f}{\partial t} = D\frac{\partial^2 c_f}{\partial x^2} - v\frac{\partial c_f}{\partial x} \qquad [6]$$

subject to

$$c_f(x,0) = f(x) - \frac{D}{v}\frac{\partial f(x)}{\partial x} \qquad [7]$$

$$c_f(0,t) = g(t) \qquad [8]$$

$$\frac{\partial c_f}{\partial x}(\ell,t) = -\frac{D}{v}\frac{\partial^2 c_r}{\partial x^2}(\ell,t) \qquad [9a]$$

$$\frac{\partial c_f}{\partial x}(\infty,t) = 0 \qquad [9b]$$

Equation [7] shows that the flux-mode initial profile will differ from the resident-mode initial profile (Eq. [2]) unless a uniform initial condition ($\partial f/\partial x = 0$) is present. The solution for c_r using a first-type instead of a third-type inlet condition (Eq. [3]) is often used to obtain c_f for a semi-infinite soil (Kreft and Zuber, 1978; Parker and van Genuchten, 1984). Equations [7] through [9b] indicate that this is only permissible for a semi-infinite soil with a uniform initial concentration. A more general approach for obtaining an expression for c_f is to use Eq. [5] to transform the solution for c_r, solved for a third-type inlet condition. Below we explore the differences between c_f and c_r obtained in this manner for nonuniform initial concentrations assuming both semi-infinite and finite soil systems.

FLUX-AVERAGED VS. RESIDENT CONCENTRATIONS

Semi-infinite System

When the solute is initially distributed between x_1 and x_2 with a unit concentration, the initial condition may be written as

$$f(x) = \begin{cases} 0 & 0 \le x < x_1 \\ 1 & x_1 \le x < x_2 \\ 0 & x_2 \le x < \infty \end{cases} \qquad [10]$$

If the input is solute-free, i.e., $g(t) = 0$, the solution for the resident concentration, c_r^{SI}, can be expressed as (van Genuchten and Alves, 1982)

$$c^{SI}(x,t) = \psi(x,t;x_1) - \psi(x,t;x_2) \qquad [11]$$

where the superscript SI is used to indicate a semi-infinite system using Eq. [4b] as the outlet condition, and where ψ for c_r is given by

$$\psi(x,t;x_i) = 1 - \frac{1}{2}\,\mathrm{erfc}\left[\frac{R(x-x_i)-vt}{\sqrt{4DRt}}\right] - \sqrt{\frac{v^2t}{\pi DR}}\exp\left\{\frac{vx}{D} - \frac{[R(x+x_i)+vt]^2}{4DRt}\right\} + \frac{1}{2}\left[1 + \frac{v(x+x_i)}{D} + \frac{v^2t}{DR}\right] \times \exp\left(\frac{vx}{D}\right)\mathrm{erfc}\left[\frac{R(x+x_i)+vt}{\sqrt{4DRt}}\right] \qquad [12]$$

Substituting Eq. [11] into Eq. [5] leads to an expression for the flux-averaged concentration, c_f^{SI}, which is also given by Eq. [11] except that ψ is now (Toride et al., 1993)

$$\psi(x,t;x_i) = 1 - \frac{1}{2}\,\mathrm{erfc}\left[\frac{R(x-x_i)-vt}{\sqrt{4DRt}}\right] - \frac{1}{2}\exp\left(\frac{vx}{D}\right)\mathrm{erfc}\left[\frac{R(x+x_i)+vt}{\sqrt{4DRt}}\right] - \sqrt{\frac{DR}{4\pi v^2t}}\left(\exp\left\{-\frac{[R(x-x_i)-vt]^2}{4DRt}\right\} - \exp\left(\frac{vx}{D}\right)\exp\left\{-\frac{[R(x+x_i)+vt]^2}{4DRt}\right\}\right) \qquad [13]$$

It is convenient to introduce the following dimensionless variables:

$$P = \frac{v\ell}{D}, \quad T = \frac{vt}{\ell} \qquad [14a,b]$$

where ℓ is now an arbitrary length (the column length in the case of a finite system), P is the Peclet number, and T is dimensionless time.

Figure 1 shows c_f^{SI} and c_r^{SI} distributions vs. relative distance, x/ℓ, at $T = 0.05$ for two values of P when solute-free water is applied to a soil having a stepwise resident initial distribution as indicated by the dashed line. For $P = 2$ (Fig. 1a), dispersive transport becomes dominant with respect to convective transport and significant spreading can be observed in c_r^{SI} in both the upstream and downstream directions. Notice that, for small T, c_f^{SI} is negative for $x \approx 0.5\ell$, and greater than unity (the initial resident concentration) for $x/\ell \approx 1$. This result is not surprising, at least in a mathematical sense,

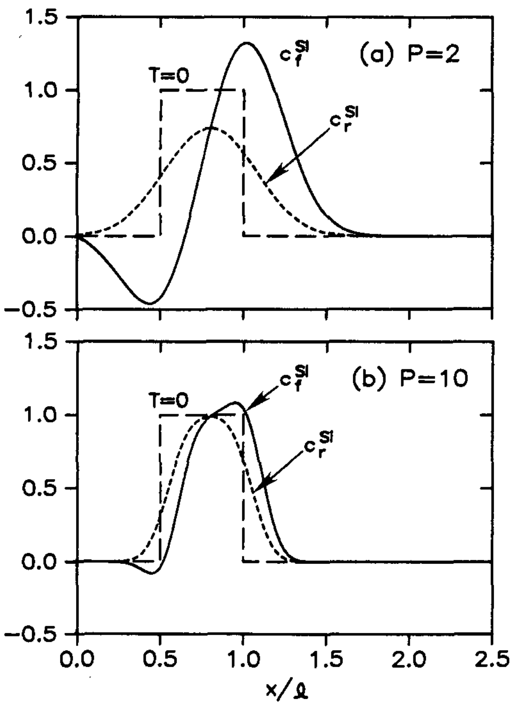

Fig. 1. Flux (c_f^{SI}) and resident (c_r^{SI}) concentrations vs. dimensionless distance, x/ℓ, for a semi-infinite system at reduced time, T = 0.05, for two values of the Peclet number (P) and a retardation factor R = 1 assuming solute-free input to a soil having a stepwise initial distribution as shown by the dashed line

if we recall the definition of c_f as given by Eq. [5], i.e., c_f is directly proportional to the solute flux J for steady water flow. Because J and the water flux, q, are vectors, c_f becomes negative when the directions of these two fluxes are opposite; this is the case when large positive gradients in c_r are present. Hence, the negative c_f near the surface is the result of an upward solute flux in spite of a downward water flux. For similar reasons, c_f becomes larger than c_r when the gradient of c_r is negative. For relatively large negative gradients such as those in Fig. 1 around $x/\ell = 1$, c_f can initially be significantly greater than the initial resident concentration $c_r(x,0)$. Notice from Fig. 1b that the differences between c_f^{SI} and c_r^{SI} become relatively small when the Peclet number increases.

We emphasize here that Fig. 1a illustrates a somewhat extreme example. First, the application of the CDE is probably questionable during the early stages of the transport process. This is because the concept of hydrodynamic dispersion may be valid only after a sufficient (travel) time has elapsed (Taylor, 1953; Jury et al., 1991, p. 218–267). Second, the only plausible physical mechanism for backward solute movement is ionic or molecular diffusion and not hydrodynamic dispersion. Finally, initial concentration distributions of the type shown in Fig. 1 may be very difficult to implement experimentally during solute displacement studies.

As mentioned above, for solute application to a semi-infinite soil with a uniform initial distribution, c_f is identical to c_r obtained for a first-type inlet condition. Except for the difficult problem of actually establishing such an inlet condition, no physically unrealistic values for c_r will occur. Because most of the literature deals with uniform initial conditions, the aforementioned anomaly in c_f has, therefore, largely been ignored.

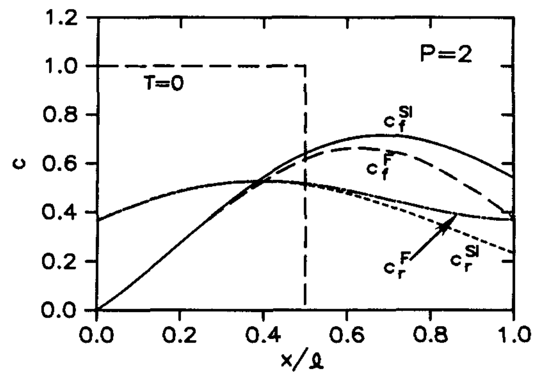

Fig. 2. Flux and resident concentrations vs. dimensionless distance, x/ℓ, for semi-infinite (c_f^{SI}, c_r^{SI}) and finite (c_f^F, c_r^F) systems at reduced time, T = 0.2, for Peclet number P = 2 and a retardation factor R = 1 assuming solute-free input to a soil having a stepwise initial distribution as shown by the dashed line.

Finite System

Van Genuchten and Parker (1984) compared c_f for a semi-infinite system with the analytical solution for a finite system, as derived by Brenner (1962), for a step input to a soil profile having a homogeneous initial condition. They concluded that c_f for semi-infinite and finite systems are almost identical at the exit, $x = \ell$, for $P > 5$. To our knowledge, no analytical solution for a finite system involving a nonuniform initial distribution has been derived. We therefore numerically calculated c_r for a finite system with the program HYDRUS of Kool and van Genuchten (1991), and subsequently evaluated c_f numerically by substituting the results for c_r into Eq. [5].

Figure 2 shows concentration profiles for four concentration modes when solute-free water is applied to a soil with a stepwise initial distribution $c_r(x,0)$ as given by the dashed line. The superscript F is used for concentrations of a finite system. Since the zero-gradient condition Eq. [4a] does not allow dispersive transport across the exit, c_r^F is greater than c_r^{SI} near the outlet. The zero-gradient condition also implies that c_f^F is always equal to c_r^F at $x = \ell$ (Eq. [5]). Finally, notice that the gradient of c_f^F at $x = \ell$ is not generally zero in accordance with Eq. [9a].

Figure 3 shows breakthrough curves for three concentration modes at $x = \ell$ when P is 1 or 5, using the same initial condition as in Fig. 2. Notice again that c_f^F and c_r^F are identical at $x = \ell$. The results also show that, when $P = 1$, c_f^{SI} is much greater than c_f^F for relatively small T, and lower than c_f^F for larger T. The differences between c_f^{SI} and c_f^F decrease for larger P but are still present when $P = 5$. The differences among the three curves depend also on the initial distribution. This is shown in Fig. 4, which presents breakthrough curves for $P = 5$ and $x = \ell$ when the initial concentration is given by

$$f(x) = \begin{cases} 1 & 0 \le x < 0.9\ell \\ 0 & 0.9\,\ell \le x \end{cases} \qquad [15]$$

Because of the extreme gradient at $x = 0.9\ell$ close to the exit boundary, the differences between c_f^{SI} and c_f^F

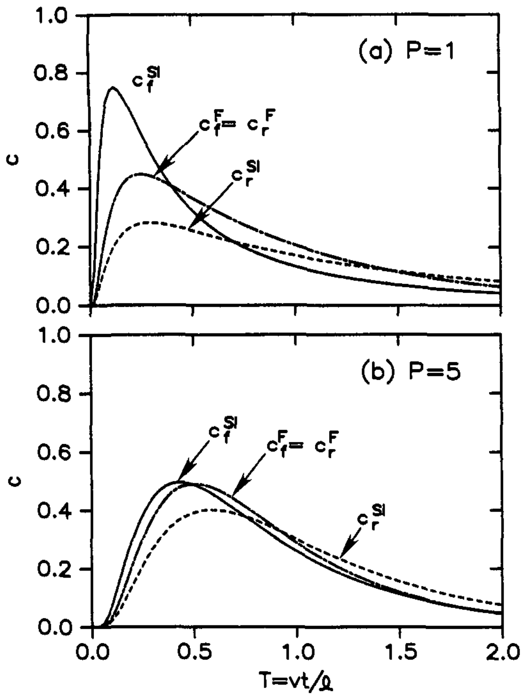

Fig. 3. Flux and resident concentrations for semi-infinite (c_f^{SI}, c_r^{SI}) and finite (c_f^F, c_r^F) systems at $x = \ell$ as a function of dimensionless time, $T = vt/\ell$, for two values of the Peclet number (P) and a retardation factor $R = 1$ assuming solute-free input to a soil having the same stepwise initial distribution as given in Fig. 2.

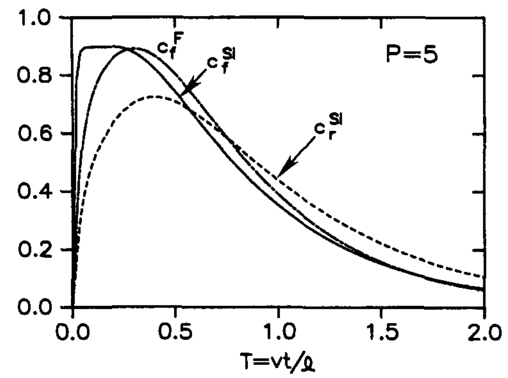

Fig. 4. Flux and resident concentrations for semi-infinite (c_f^{SI}, c_r^{SI}) and finite ($c_f^F = c_r^F$) systems at $x = \ell$ as a function of dimensionless time, $T = vt/\ell$, for Peclet number, $P = 5$ and a retardation factor $R = 1$ assuming solute-free input to a soil having a stepwise initial concentration distribution (Eq. [15]) near the exit boundary.

increase, compared with those shown in Fig. 3d, especially at relatively small times. These differences remain quite significant for P values exceeding 5.

CONCLUSIONS

This study shows that nonuniform initial conditions can significantly affect c_f distributions in both semi-infinite and finite soil systems. Because the initial and outlet conditions are influenced by the transformation from c_r to c_f, c_f is only equivalent to c_r, as derived with a first-type inlet condition, when the soil is semi-infinite and has a uniform initial condition. For stepwise resident initial distributions, c_f can be negative or greater than the initial values for c_r in the early stages of the displacement process because c_f represents a solute flux rather than a measurable concentration.

As long as the initial concentration is uniform, c_f values for semi-infinite and finite systems are almost identical at the exit. If the initial distribution involves a steep concentration gradient near the exit, however, large differences between these two concentrations can still exist for relatively large column Peclet numbers as a result of different outlet conditions. Although further investigations are still needed to find proper descriptions of the different solute detection modes and the corresponding outlet conditions, c_f for semi-infinite systems cannot be automatically applied to effluent curves for finite soil systems when a nonuniform initial solute distribution is present.

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