Mathematical Analysis of One-Dimensional Solute Transport in a Layered Soil Profile

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ABSTRACT

Solute transport studies involving layered media are important for investigating how restricting layers affect rates of solute migration in the soil profile and, more generally, for examining the influence of soil heterogeneity on solute transport. Analytical solutions of the one-dimensional advection-dispersion equation (ADE) were obtained with the help of Laplace transforms for transport in a two-layered soil profile. Assuming that the layers are, in effect, semi-infinite, solutions were obtained for first-type (constant concentration) and third-type (constant flux) conditions at both the inlet boundary and the interface of the two layers. Concentration profiles were also obtained for a finite first layer via numerical inversion of the Laplace transform solution, using a third-type condition at the inlet, and, simultaneously, a first- and third-type condition at the interface. Volume-averaged or resident-type concentrations were used in all cases. First-type conditions did not meet our criterion of mass conservation, whereas third-type conditions caused discontinuities in the concentration at the interfaces of layers with differing transport parameters. The concentration at the interface was found to be continuous, and no mass-balance error occurred, when first- and third-type conditions were imposed simultaneously at the interface. Several example calculations show the effect of soil layering on solute transport in a one-dimensional soil profile.

I NTEREST IN THE TRANSPORT of chemicals in soils is motivated by the potential of agricultural and other chemicals (fertilizers, pesticides, industrial wastes) to move from the soil surface through the unsaturated zone toward the groundwater table. The leaching of solutes in the unsaturated zone may be affected greatly by the presence of soil layers. Soil stratification is a natural phenomenon that is common to many soils. Also, artificial barriers (e.g., clay liners) are often used to slow down or prevent the movement of certain chemicals. Finally, the macroscopic impact of soil layering is important in more general studies of the effect of soil heterogeneity and anisotropy on solute transport. For example, a heterogeneous soil profile is often approximated by a series of homogeneous soil layers.

Solute transport in soils is usually described deterministically with the ADE, although alternative stochastic approaches also exist (Jury, 1982). Exact and approximate analytical solutions for transport in layered soils are now available for a limited number of situations. In most cases, however, numerical methods need to be employed. Unfortunately, compared with analytical solutions, numerical solutions frequently do not provide as much insight into the effects of physical and chemical processes on solute transport, and often are also susceptible to computational errors. Hence, analytical solutions remain useful for a variety of applications, including verification of numerical solutions.

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Past research on transport in layered soils has focused mainly on the effects of layering on solute breakthrough curves. Experimental results have been reported by Shamir and Harleman (1966), Selim et al. (1977), and Moranville et al. (1977). Theoretical analyses of solute breakthrough curves, using transfer functions and time moments, were carried out by Kreft (1981a) and Barry and Parker (1987). In many cases, however, it is also important to know the actual solute distribution in a layered profile. Analytical solutions for solute transport have been reported by Shamir and Harleman (1967), and Al-Niami and Rushton (1979). Both studies used a first-type (constant concentration) inlet condition. Shamir and Harleman (1967) assumed that the profile consisted of semi-infinite layers, while Al-Niami and Rushton (1979) used finite layers. Since only the concentration was continuous at the inlet and interfaces (Dirichlet conditions), neither solution will satisfy the principle of mass conservation at interfaces and, as a result, the applied solute mass is not equal to the mass accumulated in the soil profile. Al-Niami and Rushton (1979) also imposed the physically unrealistic assumption that the concentration gradient is zero at the interfaces of the layers.

The objective of this study was to simulate one-dimensional solute transport in a layered soil using both numerical and analytical methods. As with most previous studies, the layered profile was approximated by a series of homogeneous layers, each having its unique physical and chemical characteristics. Analytical solutions were obtained for a two-layer medium using three different combinations of inlet and interface conditions. Since the boundary and interface conditions play an important role in the solution of the ADE for layered media, the applicable boundary conditions are briefly reviewed. The effect of layering on calculated solute concentrations in a layered soil profile is illustrated qualitatively, using both analytical and numerical solutions.

THEORY

Analytical Solution for a Two-Layer Medium

Figure 1 schematically shows a layered soil, consisting of two homogeneous layers, during steady water flow perpendicular to the interface of the two layers. The first layer is located between $x = 0$ and $x = L$, and the second layer between $x = L$ and infinity. Transport of a linearly exchanging solute in both layers is described with the ADE:

$$R_k \frac{\partial C_k}{\partial t} = D_k \frac{\partial^2 C_k}{\partial x^2} - v_k \frac{\partial C_k}{\partial x} \qquad t > 0 \qquad [1]$$

where R is the retardation factor, C is the resident concentration expressed in mass of solute per volume of solution [M L^{-3}], t is time [T], D is the dispersion coefficient [L^2 T^{-1}], v is the mean pore-water velocity [L T^{-1}], x is distance in the direction of flow [L], and the subscript k refers to the soil layer ($k = 1,2$). We emphasize that, in this study, C represents volume-averaged or resident concentrations (van Genuchten and Parker, 1984) rather than flux-averaged concentrations as employed by Barry and Parker (1987). Volume- and flux-averaged concentrations are related according to (e.g., Kreft and Zuber, 1978)

$$vC^F = vC - D\frac{\partial C}{\partial x} \qquad [2]$$

where the superscript F denotes a flux-averaged value.

The dispersion coefficient D in Eq. [1] reflects two mechanisms responsible for solute spreading, molecular diffusion and mechanical dispersion. A common expression for the dispersion coefficient is

$$D = \lambda D_o + \alpha|v| \qquad [3]$$

where D_o is the ionic or molecular diffusion coefficient in free water [L^2T^{-1}], λ is a tortuosity factor ($0 < \lambda < 1$), and α is the dispersivity [L]. Equation [3] assumes that, macroscopically, the active process of diffusion can be combined with the more passive process of mechanical dispersion. It is unlikely that this assumption correctly describes the microscopic diffusion-dispersion process in the vicinity of interfaces. Hence, the ADE as given by Eq. [1] can, at best, approximate solute transport in the neighborhood of interfaces.

Two different approaches were used to solve Eq. [1] analytically. In one approach, we assumed that each homogeneous layer is part of an effectively semi-infinite system. This approach assumes that concentrations in the first layer are not affected by the presence of a second layer and, hence, that analytical solutions for homogeneous media can be applied immediately to the first layer. Barry and Parker (1987) derived conditions that indicate that this approach is justified in most cases. Transport in the second layer was solved for a first- or third-type condition at the interface of the two soil layers using the solute concentration of the first layer as the inlet condition for the second layer. In concept, this approach is relatively straightforward and can be extended to any desired number of layers (although the solution process becomes more tedious when the number of layers increases).

In the second approach, we assumed that the first layer was finite. The interface conditions were then formulated so that solute fluxes *and* solute concentrations became continuous. This approach caused the concentration of the first layer to become dependent on the transport properties of the second layer. Both approaches are discussed separately below.

Semi-infinite First Layer

The initial condition imposed on Eq. [1] is

$$C_1(x,0) = g_1 \qquad 0 < x < L \qquad [4]$$

where g_1 is assumed to be a constant. For the inlet boundary at $x = 0$, we imposed step functions of duration t_o using either a first-type condition of the form

$$C_1|_{x|0} = \begin{cases} C_o & 0 < t \le t_o \\ 0 & t > t_o \end{cases} \qquad [5]$$

or a third-type condition

$$\left(v_1 C_1 - D_1 \frac{\partial C_1}{\partial x}\right)\bigg|_{x|0} = \begin{cases} v_1 C_o & 0 < t \le t_o \\ 0 & t > t_o \end{cases} \qquad [6]$$

where $x|0$, sometimes denoted also as $x\rightarrow0^+$, implies that $x = 0$ is approached from inside the soil profile. The physical basis of Eq. [5] and [6] has been discussed at length in the literature (e.g., Danckwerts, 1953; Wehner and Wilhelm, 1956; Pearson, 1958; Kreft and Zuber, 1978; van Genuchten and Parker, 1984). Adoption of a first-type condition always leads to continuity in the resident concentration, whereas a third-type condition always leads to continuity in the solute flux. Because of these properties, the first-type condition is also known as a concentration-type condition, and the third-type condition as a flux-type condition. The latter condition
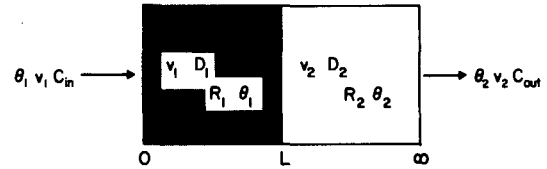

Fig. 1. Schematic of transport in a two-layer medium (θ = volumetric water content, v = pore-water velocity, C_{in} = concentration of the incoming solution, D = dispersion coefficient, R = retardation factor, and C_{out} = concentration of the effluent).

is the more appropriate one for solute displacement experiments (van Genuchten and Parker, 1984). Because solutions obtained with a first-type condition are useful for situations where the concentration is measured as a flux-averaged value (e.g., for column effluent curves), we also considered the first-type boundary condition. We noted that adoption of the third-type condition leads to a macroscopic discontinuity of the (volume-averaged) resident concentration at the inlet, even though, microscopically, the concentration distribution may remain continuous for all times $t > 0$ (see discussions by Dagan and Bresler, 1985; Parker and van Genuchten, 1985). This discontinuity results from the simplifying assumptions that (i) the incoming solution is well mixed and has a constant concentration, and (ii) the dispersion coefficient at or immediately below the soil surface is the same as that of the soil profile farther away from the inlet boundary.

If we assume that the concentration of the first layer is unaffected by the second layer, then one can readily invoke boundary conditions for homogeneous media at the outlet of that first layer. A commonly used condition assumes that the concentration is macroscopically continuous across the outlet boundary, at $x = L$:

$$\frac{\partial C_1}{\partial x}\bigg|_{x|L} = 0 \qquad t > 0 \qquad [7]$$

However, it is difficult to imagine how dispersive transport between two layers will vanish during transient advective transport across the outlet boundary. Alternatively, the presence of an effectively semi-infinite medium could be invoked by imposing the condition

$$\frac{\partial C_1}{\partial x}\bigg|_{x\rightarrow\infty} = 0 \qquad t > 0 \qquad [8]$$

Because of considerations outlined in detail by van Genuchten and Parker (1984), and because of possible mathematical simplifications later, we decided to use Eq. [8] for our analytical solutions. We emphasize that, at least for homogeneous soils, differences between solutions for finite and semi-infinite media are usually rather small (van Genuchten and Alves, 1982).

The analytical solution of Eq. [1] subject to Eq. [4] and [8] for a first- or third-type condition at the inlet is:

$$C_1(x,t) = \begin{cases} g_1 + (C_o - g_1)A(x,t) & 0 < t \le t_o \\ g_1 + (C_o - g_1)A(x,t) & \\ \quad - C_o A(x,t - t_o) & t > t_o \end{cases} \qquad [9]$$

where, for a first-type condition (Lapidus and Amundson, 1952),

$$A(x,t) = \frac{1}{2}\operatorname{erfc}\left[\frac{R_1 x - v_1 t}{(4D_1 R_1 t)^{1/2}}\right]$$

$$+ \frac{1}{2}\exp\left(\frac{v_1 x}{D_1}\right)\operatorname{erfc}\left[\frac{R_1 x + v_1 t}{(4D_1 R_1 t)^{1/2}}\right] \qquad [10]$$

and, for a third-type condition (Lindstrom et al., 1967),

$$A(x,t) = \frac{1}{2} \text{erfc} \left[\frac{R_1 x - v_1 t}{(4D_1 R_1 t)^{1/2}} \right]$$

$$+ \left(\frac{v_1^2 t}{\pi D_1 R_1} \right)^{1/2} \exp\left(- \frac{(R_1 x - v_1 t)^2}{4D_1 R_1 t} \right)$$

$$- \frac{1}{2} \left(1 + \frac{v_1 x}{D_1} + \frac{v_1^2 t}{D_1 R_1} \right)$$

$$\times \exp\left(\frac{v_1 x}{D_1} \right) \text{erfc} \left[\frac{R_1 x + v_1 t}{(4D_1 R_1 t)^{1/2}} \right] \quad [11]$$

Analytical solutions for the second layer were obtained with the following boundary and initial conditions:

$$C_2(x,0) = g_2 \qquad x > L \qquad [12]$$

$$C_1|_{x \downarrow L} = C_2|_{x \downarrow L} \qquad \text{(first type)} \qquad [13]$$

or

$$\left(\theta_1 v_1 C_1 - \theta_1 D_1 \frac{\partial C_1}{\partial x} \right) \bigg|_{x \downarrow L}$$

$$= \left(\theta_2 v_2 C_2 - \theta_2 D_2 \frac{\partial C_2}{\partial x} \right) \bigg|_{x \downarrow L} \qquad \text{(third type)} \qquad [14]$$

$$\frac{\partial C_2}{\partial x} \bigg|_{x \to \infty} = 0 \qquad [15]$$

where θ is the volumetric water content and g_2 is assumed to be constant. Interface Condition [13] is used in conjunction with Eq. [9] and [10] while Condition [14] is applied with Eq. [9] and [11]. Notice that Eq. [13] implies that the concentration is continuous across the interface, while Eq. [14] implies that the solute flux is continuous.

The analytical solution of Eq. [1] with $k = 2$, subject to Conditions [12], [13], and [15] for the first-type inlet and interface conditions, was obtained by Laplace transformation (for details, see Leij and Dane, 1989). The solution may be written in the form

$$C_2(x,t) = \begin{cases} (C_o - g_1)A(x,t) \\ \quad + (g_1 - g_2)B(x,t) + g_2 & 0 < t \leq t_o \\ (C_o - g_1)A(x,t) - C_oA(x, t - t_o) \\ \quad - (g_1 - g_2)B(x,t) + g_2 & t > t_o \end{cases} \quad [16]$$

where

$$A(x,t) = \frac{x - L}{4(\pi D_2/R_2)^{1/2}} \int_0^t \left\{ \text{erfc} \left[\frac{R_1 L - v_1 \tau}{(4R_1 D_1 \tau)^{1/2}} \right] \right.$$

$$+ \exp\left(\frac{v_1 L}{D_1} \right) \text{erfc} \left[\frac{R_1 L + v_1 \tau}{(4R_1 D_1 \tau)^{1/2}} \right] \right\} \times \left\{ (t - \tau)^{-3/2} \right.$$

$$\exp\left[- \left(\frac{R_2(x - L) - v_2(t - \tau)}{4R_2 D_2(t - \tau)} \right)^2 \right] \right\} d\tau \quad [17a]$$

$$B(x,t) = \frac{1}{2} \text{erfc} \left[\frac{R_2 (x - L) - v_2 t}{(4R_2 D_2 t)^{1/2}} \right]$$

$$+ \frac{1}{2} \exp\left(\frac{v_2(x - L)}{D_2} \right) \text{erfc} \left[\frac{R_2 (x - L) + v_2 t}{(4R_2 D_2 t)^{1/2}} \right] \quad [17b]$$

where τ is an integration variable. Similarly, the solution of Eq. [1], [12], [14], and [15] for third-type conditions is given by Eq. [16] with

$$A(x,t) = \frac{v_2}{(4R_2 D_2)^{1/2}} \int_0^t \left\{ \text{erfc} \left[\frac{R_1 L - v_1 \tau}{(4R_1 D_1 \tau)^{1/2}} \right] \right.$$

$$+ \exp\left(\frac{v_1 L}{D_1} \right) \text{erfc} \left[\frac{R_1 L + v_1 \tau}{(4R_1 D_1 \tau)^{1/2}} \right] \right\}$$

$$\times \left(\pi(t - \tau)^{-1/2} \exp\left\{ - \frac{[R_2(x - L) - v_2(t - \tau)]^2}{4R_2 D_2 (t - \tau)} \right\} \right.$$

$$- \frac{v_2}{(4R_2 D_2)^{1/2}} \exp\left[\frac{v_2(x - L)}{D_2} \right]$$

$$\times \text{erfc}\left\{ \frac{R_2(x - L) + v_2 (t - \tau)}{[4R_2 D_2 (t - \tau)]^{1/2}} \right\} \right) d\tau \quad [18a]$$

$$B(x,t) = \left(\frac{v_2^2 t}{\pi R_2 D_2} \right)^{1/2} \exp\left\{ - \frac{[R_2 (x - L) - v_2 t]^2}{4R_2 D_2 t} \right\}$$

$$+ \frac{1}{2} \text{erfc} \left[\frac{R_2 (x - L) - v_2 t}{(4R_2 D_2 t)^{1/2}} \right]$$

$$+ \frac{1}{2} \left(1 + \frac{v_2 (x - L)}{D_2} + \frac{v_2^2 t}{R_2 D_2} \right)$$

$$\exp\left[\frac{v_2(x - L)}{D_2} \right] \text{erfc} \left[\frac{R_2 (x - L) + v_2 t}{(4R_2 D_2 t)^{1/2}} \right] \quad [18b]$$

The integrals appearing in these solutions were evaluated with the help of the Gauss-Chebyshev formula (see Appendix A). Equations [17] and [18] show that transport properties of both layers influence the solute concentrations of the second layer.

The above solutions hold for a two-layer soil profile. Laplace domain solutions are easily obtained for profiles consisting of more than two layers. Consider step displacement $(t_o \to \infty)$ in a medium containing n homogeneous layers with uniform initial concentration, g, in the entire profile. For first-type conditions at the interfaces of two consecutive layers, the Laplace solution for layer k is

$$\overline{C}_k (x,s) = \frac{C_o - g}{s} \exp\left(\sum_{j=1}^{k-1} \lambda_j l_j \right)$$

$$\exp\left[\lambda_k (x - L_{k-1}) \right] + \frac{g}{s} \qquad (1 < k \leq n) \quad [19]$$

and, for third-type conditions,

$$\overline{C}_k (x,s) = \frac{v_k}{s} \frac{C_o - g}{(v_k - D_k \lambda_k)}$$

$$\exp\left(\sum_{j=1}^{k-1} \lambda_j l_j \right) \exp\left[\lambda_k (x - L_{k-1}) \right] + \frac{g}{s} \quad [20]$$

where s is the Laplace transform variable, l is the length of layer j, L_{k-1} is the distance from the inlet to the interface between layers $k - 1$ and k, and

$$\lambda_j = \frac{v_j}{2D_j} - \left[\left(\frac{v_j}{2D_j} \right)^2 + \frac{sR_j}{D_j} \right]^{1/2} \quad [21]$$

Solutions in the real time domain are complicated, but can be formally obtained by making use of the convolution theorem. The important points illustrated by Eq. [19] and [20] are that (i) the order of the soil layers from layer 1 to $k - 1$ is irrelevant when calculating the solute concentration of layer k, and (ii) the concentration of any layer k is not affected by any layer beyond k. Similar conclusions were obtained by Shamir and Harleman (1967), Selim et al., (1977), and Barry and Parker (1987).

Finite First Layer

If we deal with resident concentrations, mass conservation will require that the solute flux be continuous across the interface. In addition, one could reason that the concentration across the interface must be continuous as well, at least microscopically, because of the impact of ionic or molecular diffusion. The transport problem where both the flux and the concentration are continuous resembles the problem of heat flow in composite media with no contact resistance at the interface (Carslaw and Jaeger, 1959), and was applied previously to steady-state solute transport by Wehner and Wilhelm (1956). Rather than assuming that the first layer is part of an effectively semi-infinite system, the two interface conditions now serve as an outlet condition for the first layer and an inlet condition for the second layer (Kreft, 1981b). Consequently, Eq. [1] was solved subject to the following conditions

$$C_1 (x,0) = g_1 \qquad 0 < x < L \qquad [22]$$

$$C_2 (x,0) = g_2 \qquad x > L \qquad [23]$$

$$\left(v_1 C_1 - D_1 \frac{\partial C_1}{\partial x} \right) \bigg|_{x \downarrow 0}$$

$$= \begin{cases} v_1 C_0 & 0 < t \le t_0 \\ 0 & t > t_0 \end{cases} \qquad [24]$$

$$C_1|_{x \uparrow L} = C_2|_{x \downarrow L} \qquad t > 0 \qquad [25]$$

$$\left(\theta_1 v_1 C_1 - \theta_1 D_1 \frac{\partial C_1}{\partial x} \right) \bigg|_{x \uparrow L}$$

$$= \left(\theta_2 v_2 C_2 - \theta_2 D_2 \frac{\partial C_2}{\partial x} \right) \bigg|_{x \downarrow L} \qquad t > 0 \qquad [26]$$

$$\frac{\partial C_2}{\partial x} \bigg|_{x \to \infty} = 0 \qquad t > 0 \qquad [27]$$

Equations [25] and [26] stipulate continuity in concentration and flux across the interface. Using Eq. [25], the third-type interface condition can also be written as a second-type (Neumann) condition:

$$\theta_1 D_1 \frac{\partial C_1}{\partial x} \bigg|_{x \uparrow L} = \theta_2 D_2 \frac{\partial C_2}{\partial x} \bigg|_{x \downarrow L}$$

$$t > 0 \quad \text{(second type)} \qquad [28]$$

The analytical solution of the problem, subject to Eq. [22] to [27], is considerably more difficult than the previous solutions for either the first-type or third-type inlet and interface conditions. The solution in the Laplace domain is

$$\overline{C}_1 (x,s) = \frac{g_1}{s}$$

$$+ \frac{C_0 - g_1 - C_0 \exp(-t_0 s)}{\left(\frac{1}{2} - q_1 \right)(q_1 - q_2) \exp(-\omega_1 L) + \left(\frac{1}{2} + q_1 \right)(q_1 + q_2) \exp(\omega_1 L)}$$

$$\times \frac{1}{s} \left\{ (q_1 - q_2) \exp\left[\frac{v_1 x}{2D_1} + \omega_1(x - L) \right] \right.$$

$$\left. + (q_1 + q_2) \exp\left[\frac{v_1 x}{2D_1} - \omega_1(x - L) \right] \right\} \qquad [29]$$

$$\overline{C}_2(x,s) = \frac{g_2}{x}$$

$$+ \frac{2q_1[C_0 - g_1 - C_0 \exp(-t_0 s)] \exp(v_1 L/2D_1)}{\left(\frac{1}{2} - q_1 \right)(q_1 - q_2) \exp(-\omega_1 L) + \left(\frac{1}{2} + q_1 \right)(q_1 + q_2) \exp(\omega_1 L)}$$

$$\times \left\{ \frac{1}{s} \exp\left[\frac{v_2 (x - L)}{2D_2} - \omega_2 (x - L) \right] \right\} \qquad [30]$$

where

$$\omega_j = \left[\left(\frac{v_j}{2D_j} \right)^2 + \frac{sR_j}{D_j} \right]^{1/2} \qquad [31]$$

$$q_j = (D_j \omega_j)/v_j \qquad [32]$$

Note that the concentration profile in the first layer now depends on the transport properties of the second layer. Attempts to analytically invert Eq. [29] and [30] were not successful. Instead, we obtained concentration profiles using numerical inversion of the Laplace transform according to the method of Crump (1976). The solution in the Laplace domain can also be readily used for time moment analysis (e.g., Kreft, 1981a). Finally, we note that the two-layer solution given by Eq. [29] and [30] provides a method for examining concentration profiles at the inlet and outlet boundaries of a homogeneous medium by adopting appropriately small values for D_1 and D_2, respectively (see also Wehner and Wilhelm, 1956; Pearson, 1958).

Numerical Solution for a Layered Medium

Analytical solutions are often not available, or cannot be derived (e.g., for nonlinear sorption or time-dependent boundary conditions), in which case, numerical methods must be employed. In this section, we briefly outline the mathematical problem and its solution. For a soil column consisting of n layers, Eq. [1] was solved for the following conditions:

$$C_k (x,0) = g_k \qquad 0 < x < L_n \qquad [33]$$

$$\left(-D_1 \frac{\partial C_1}{\partial x} + v_1 C_1 \right) \bigg|_{x \downarrow 0} = v_1 C_0(t) \qquad t > 0 \qquad [34]$$

$$(\theta D)_k \frac{\partial C_k}{\partial x} \bigg|_{x \uparrow L_k}$$

$$= (\theta D)_{k+1} \frac{\partial C_{k+1}}{\partial x} \bigg|_{x \downarrow L_k} \quad \begin{array}{l}\text{(second type)} \\ k = 1,2 \ldots n\end{array} \qquad [35]$$

or

$$\left[(\theta vC)_k - \left(\theta D \frac{\partial C}{\partial x} \right)_k \right] \Bigg|_{x \uparrow L_k}$$

$$= \left[(\theta vC)_{k+1} - \left(\theta D \frac{\partial C}{\partial x} \right)_{k+1} \right] \Bigg|_{x \downarrow L_k}$$

(third type)　　　　　　[36]

$$\frac{\partial C_n}{\partial x} \Bigg|_{x \uparrow L_n} = 0 \qquad t > 0 \qquad [37]$$

Note that only one condition is needed at each interface, i.e., either Eq. [35] or [36]. Equation [1], subject to Eq. [33] through [37], was solved numerically using an implicit Crank-Nicolsen-type finite-difference method. Details of the numerical solution are given by Leij and Dane (1989).

RESULTS AND DISCUSSION

Several examples are presented to illustrate the effects of layering and the use of different boundary conditions on computed solute distributions. First, we assessed the magnitude of mass-balance errors associated with the three analytical solutions that were derived for the two-layer medium. A second example shows concentration profiles obtained analytically for a two-layer medium having layers with different advective and dispersive properties. A third example considers two different scenarios for reducing contaminant transport in a soil profile. Concentration profiles for this last example were obtained numerically. Table 1 lists numerical values of the transport parameters used for these examples.

Analytical Solutions for a Two-Layer Medium

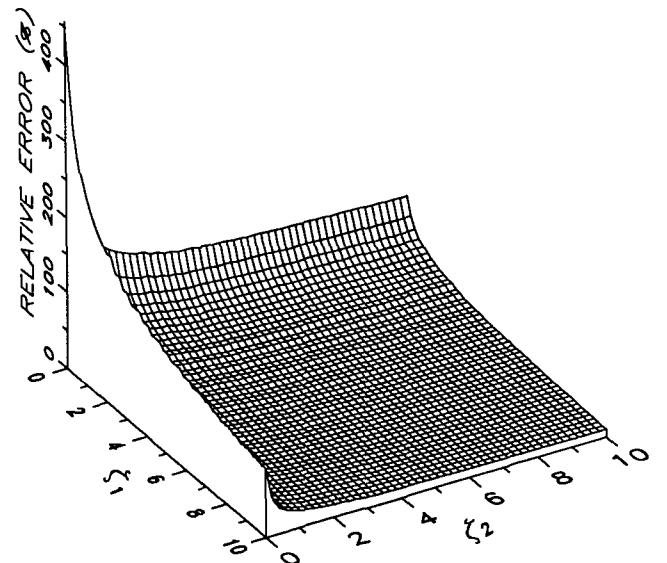Appendix B describes how the mass-balance error is defined and how errors are obtained for the three

Table 1. List of transport parameters for the simulations (v = pore-water velocity, D = dispersion coefficient, θ = volumetric water content, and R = retardation factor).†

Fig.	Layer (k)	v	D	θ	R
		cm/d	cm/d²		
3a	1	10	40	0.4	1.0
	2	10	5	0.4	1.0
3b	1	10	5	0.4	1.0
	2	10	40	0.4	1.0
4a	1	50	20	0.2	1.0
	2	20	20	0.5	1.0
4b	1	20	20	0.5	1.0
	2	50	20	0.2	1.0
5a	1	100	52	0.4	4.25
	2	100	52	0.4	4.25
	3	100	52	0.4	4.25
5b	1	10	7	0.4	4.25
	2	8	18	0.5	14.0
	3	10	7	0.4	4.25
5c	1	10	7	0.4	4.25
	2	8	18	0.5	14.0
	3	10	7	0.4	4.25
6a	1	10	7	0.2	7.5
	2	10	7	0.2	7.5
	3	10	7	0.2	7.5
6b	1	1	4	0.2	7.5
	2	0.5	2.5	0.4	1.0
	3	1	4	0.2	7.5
6c	1	1	4	0.2	7.5
	2	0.5	2.5	0.4	1.0
	3	1	4	0.2	7.5

† g_k/C_o = 0.05, (g_k is the initial concentration of layer k and C_o is the concentration of the incoming solute pulse).

analytical solutions. These errors were obtained by comparing the amount of solute accumulated in the soil profile with the cumulative solute flux entering the soil (van Genuchten and Parker, 1984). The solutions are distinguished according to the invoked interface condition, i.e., a first-type solution, given by Eq. [9], [10], [16], and [17]; a third-type solution given by Eq. [9], [11], [16], and [18]; and a combined first- and third-type solution given by Eq. [29] and [30]. For a third-type condition, the relative error was exactly zero, whereas, for a combined first- and third-type condition, the error was found to be almost zero ($<$0.1%) due to approximations involving the numerical inversion of the Laplace transform. The error associated with the first-type boundary and interface conditions in terms of dimensionless parameters is (see Appendix B):

$$E_r = \frac{1}{(\pi \zeta_1)^{1/2}} \exp\left(-\frac{\zeta_1}{4} \right) \left[1 - \exp\left(\frac{P}{2} - \frac{P^2}{4\zeta_1} \right) \right]$$

$$+ \frac{1}{\zeta_1} - \left(\frac{1}{\zeta_1} + \frac{1}{2} \right) \mathrm{erfc}\left(\frac{1}{2} \sqrt{\zeta_1} \right)$$

$$+ \frac{1}{2\zeta_1} \exp(P) \, \mathrm{erfc}\left(\frac{P + \zeta_1}{2\sqrt{\zeta_1}} \right) - (1 - P + \zeta_1)$$

$$\mathrm{erfc}\left(\frac{P - \zeta_1}{2\sqrt{\zeta_1}} \right) + \frac{1}{2\zeta_1} \int_0^{\zeta_1} \left\{ \exp(P) \, \mathrm{erfc}\left[\frac{P + \zeta_1 - y}{2(\zeta_1 - y)^{1/2}} \right] \right.$$

$$\left. + \mathrm{erfc}\left[\frac{P - \zeta_1 - y}{2(\zeta_1 - y)^{1/2}} \right] \right\}$$

$$\times \left\{ 1 - \frac{1}{2} \mathrm{erfc}\left[\left(\frac{y\zeta_2}{4\zeta_1} \right)^{1/2} \right] \right.$$

$$\left. + \left(\frac{\zeta_1}{\pi \zeta y} \right)^{1/2} \exp\left(-\frac{y\zeta_2}{4\zeta} \right) \right\} dy \qquad [38]$$

Fig. 2. Relative mass-balance error as a function of the dimensionless times ζ_1 and ζ_2 for the analytical solution of transport in a two-layer medium using a first-type condition.

where the dimensionless time $\zeta_k = v_k^2 t/(R_k D_k)$ and the Peclet number $P = v_1 L/D_1$. For the one-layer case $(L \to \infty)$, E_r reduces to Eq. [10] of van Genuchten and Parker (1984). We note that, if the solute influx were determined just inside the porous medium as the sum of the advective and dispersive fluxes, the error resulting from the inlet boundary would be equal to zero because of the mass-conserving nature of the ADE (first-type conditions at the interface of soil layers would still lead to errors). Although the use of such an error criterion seems attractive for mathematical reasons, the solute influx just inside the medium may provide an incorrect estimate of the actual (physical) solute flux just outside the medium, since no flux continuity is mandated for a first-type inlet condition. Figure 2 shows E_r (%) vs. the dimensionless parameter ζ_k for both layers. The error is largest for small values of ζ_1 and ζ_2, with ζ_1 having a slightly larger effect on the error than ζ_2. If $\zeta_1 = \zeta_2$, we obtain Fig. 1 of van Genuchten and Parker (1984).

Figures 3 and 4 show calculated solute distributions for transport of a nonreactive solute ($R = 1$) in a two-layer medium at various times for different values of D and v. Relatively large differences in D and v were used to illustrate the effects of soil layering. The types of inlet and interface conditions are specified in the figures (note that a third-type soil surface condition was always used in conjunction with a combined first- and third-type interface condition). The value of D for the first layer of Fig. 3a is larger than that of the second

layer, whereas the opposite is true for Fig. 3b. This causes the concentration profile in Fig. 3a to become steeper in the second than in the first layer, whereas in Fig. 3b the reverse can be observed. Previous studies (e.g., van Genuchten and Parker, 1984) and Eq. [38] showed that a first-type condition at the inlet boundary introduces a mass-balance error that depends on the values for D and v. This error is proportional to D and can be evaluated qualitatively by comparing the first- with the third-type solution. Figures 3a and b show that the largest errors occur in the first and second layer, respectively.

A discontinuity in concentration develops when a third-type interface condition is used. This situation is similar to the inlet boundary where the flux-averaged concentration is continuous, and the resident concentration discontinuous. From Eq. [2] and [14], it follows that flux-averaged concentrations are continuous at the interface. Finally, the solution for a combined first- and third-type condition at the interface exhibits both mass conservation and continuity of the (resident) solute concentration. The differences between the solute profiles in the first layer for third- and combined first- and third-type conditions show the influence of the second layer on transport in the first layer (Fig. 3a). The differences in concentration are less pronounced for lower values of D in the first layer (Fig. 3b).

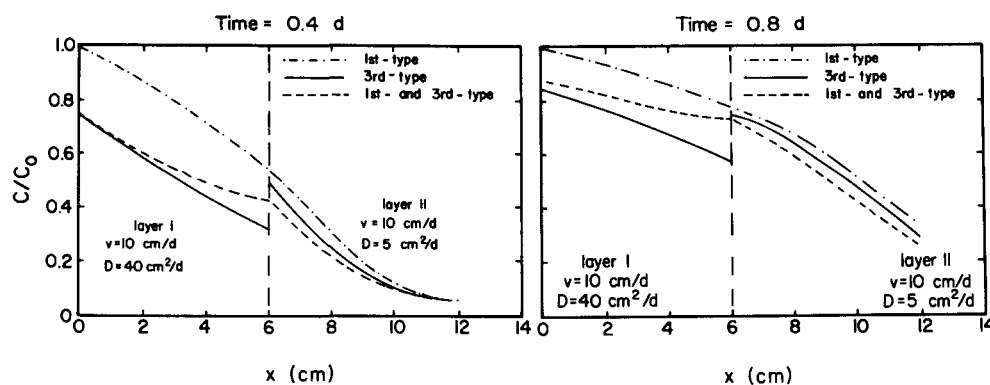The effect of different values for v on concentration profiles during steady flow are shown in Fig. 4. In Fig.

Fig. 3a. Relative concentration (C/C_0) as a function of distance (x) for the analytical solution of the advection-dispersion equation for a two-layer medium with $v_1 = v_2$ (v = pore-water velocity) and $D_1 > D_2$ (D = dispersion coefficient) at two different times using three different interface conditions.
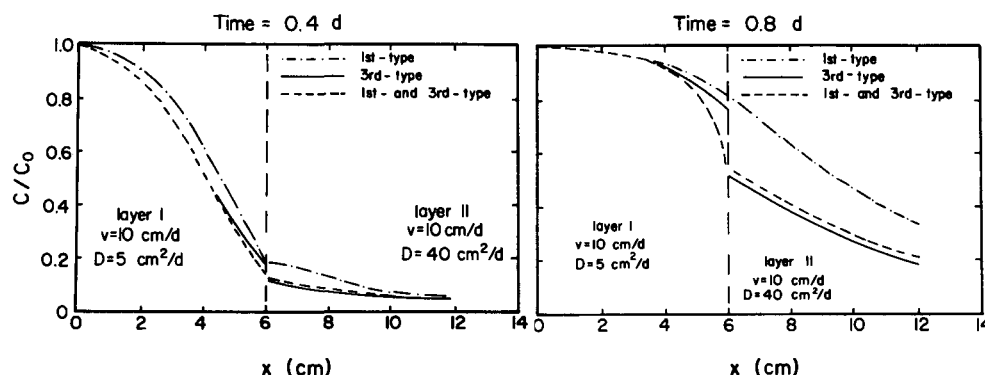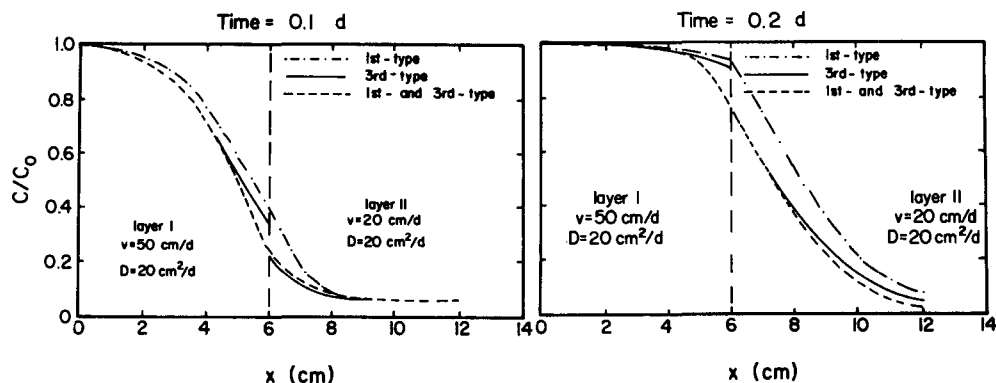

Fig. 3b. Relative concentration (C/C_0) as a function of distance (x) for the analytical solution of the advection-dispersion equation for a two-layer medium with $v_1 = v_2$ (v = pore-water velocity) and $D_1 < D_2$ (D = dispersion coefficient) at two different times using three different interface conditions.

Fig. 4a. Relative concentration (C/C_o) as a function of distance (x) for the analytical solution of the advection-dispersion equation for a two-layer medium with $D_1 = D_2$ (D = dispersion coefficient) and $v_1 > v_2$ (v = pore-water velocity) at two different times using three different interface conditions.
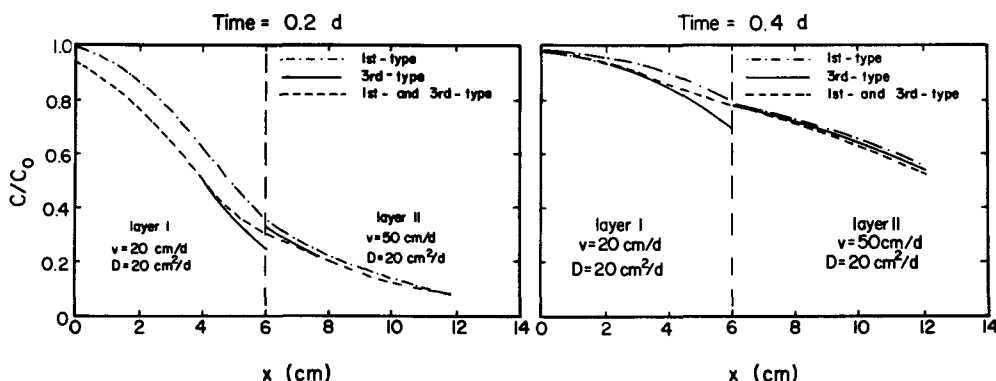

Fig. 4b. Relative concentration (C/C_o) as a function of distance (x) for the analytical solution of the advection-dispersion equation for a two-layer medium with $D_1 = D_2$ (D = dispersion coefficient) and $v_1 < v_2$ (v = pore-water velocity) at two different times using three different interface conditions.

4a, the pore-water velocity is largest in the first layer, while in Fig. 4b the second layer has the larger velocity. The solute front is steeper at the interface in the low-velocity layer. The mass-balance error associated with the first-type condition can again be evaluated by comparison with the third-type condition. This error is inversely proportional to v. For a third-type condition, the concentration at the interface is lowest in the low-velocity layer. The values of the advective and dispersive fluxes are, respectively, lower and higher in the low-velocity layer than in the high-velocity layer because of the differences in θ. We note again that, for a third-type condition, the flux-averaged concentration is continuous at the interface. The differences between the third- and the combined first- and third-type conditions are minor except in the vicinity of the interface. The analytical solution for a third-type condition can, therefore, be used in many instances, rather than the more complicated solution for a combined first- and third-type condition, which requires numerical inversion of the Laplace transform.

Numerical Solutions for a Three-Layer Medium

The next two examples are meant to illustrate the effect of a "barrier" on contaminant transport. Concentration profiles were obtained numerically using a

third-type condition at the inlet and a second- or third-type condition at the interface.

Consider a homogeneous sandy soil with a low value for R, which is saturated or close to fluid saturation. Figure 5a shows calculated solute distributions for this profile, using the parameter values listed in Table 1. Transport of the solute can be slowed by incorporating a fine-textured layer that reduces the solute flux by decreasing the water flow rate and increasing adsorption. Figure 5 shows the effect on the solute-concentration profiles of embedding a 2-cm-thick clay layer in the otherwise homogeneous profile. Results are for third-type (Fig. 5b) and second-type (Fig. 5c) conditions at the interface of the soil layers. The presence of the clay layer was assumed to result in a tenfold reduction of v (Table 1). The value of D was calculated according to Eq. [3], using $\lambda D_o = 2$ cm²/d, while α was assumed equal to 0.5 cm for the sand and 2 cm for the clay.

Figure 5b shows that the concentration in the clay layer is considerably lower than in the sand layer at both interfaces. This is caused by the use of two different parameter values in the ADE at the interface (i.e., different values for D/R and v/R). One could argue that, at least microscopically, the concentration in the liquid phase should be continuous at the interface. The use of a second-type condition is, therefore, preferred, although the profiles in Fig. 5b and c are very
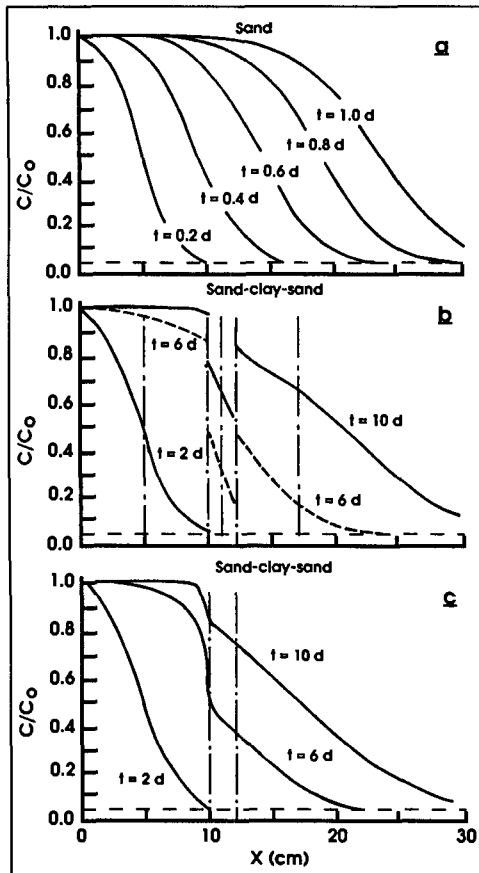
Fig. 5. Relative concentration (C/C_o) as a function of distance (x) for different times (t) in (a) a hypothetical sand without a clay layer, (b) with a hypothetical clay layer and a third-type condition, and (c) with a clay layer and a second-type condition.

Fig. 6. Relative concentration (C/C_o) as a function of distance (x) for different times (t) in (a) a hypothetical clay without a sand layer, (b) with a hypothetical sand layer and a third-type condition, and (c) with a sand layer and a second-type condition.

similar, except for the clay layer. Locations of the front for zero dispersion (shown by the five vertical dashed lines in Fig. 5b) were included to show the effectiveness of the added adsorption capacity of the clay layer. The resulting step fronts correspond to times of 2, 4.25, 6, 7.75, and 10 d. The solute moves more slowly through the sand when no dispersion occurs. Because of dispersion, the adsorption capacity of the clay layer is not fully utilized. This example shows that the magnitude of the dispersion coefficient needs to be known for accurately predicting solute movement under these conditions.

Figure 5 showed results for situations where a fine-textured layer may retard solute transport in an otherwise coarse-textured, relatively wet soil. Solute transport may also be slowed by including a coarse-textured layer in a relatively dry porous medium (Winograd, 1974). Figure 6 compares concentration profiles for a homogeneous clay (Fig. 6a) with those for a clay–sand–clay system using either a third-type (Fig. 6b) or a second-type (Fig. 6c) condition at the interface of the soil layers; a third-type condition was always used at the inlet of the soil. The inclusion of the sand layer was assumed to result in a tenfold reduction of the water flow rate (Table 1) because of the low hydraulic conductivity of the sand. Since adsorption is now absent, the rate of solute movement is reduced to a lesser
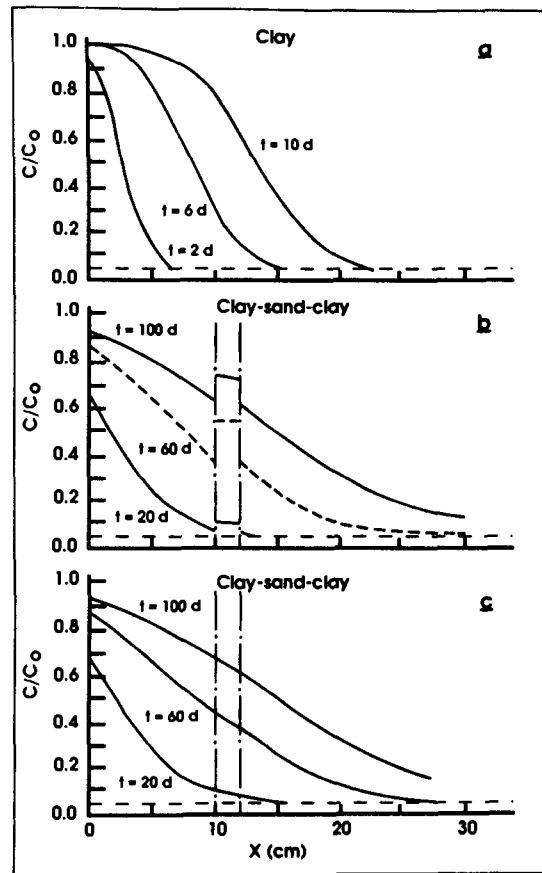
extent. Because of the lower value of P for the three-layer system, considerable time is needed for the inlet concentration to become equal to the input concentration. Notice that the discontinuity at the interface behaves in an opposite manner than for the clay layer in the previous example.

CONCLUSIONS

Analytical solutions of the one-dimensional ADE were obtained for transport in a two-layer medium assuming both a first- and a third-type condition at the inlet boundary and the soil interface. Both layers were assumed to be part of a semi-infinite system. In addition, concentration profiles were obtained for a combined first- and third-type condition at the interface, and a third-type condition at the inlet, using numerical inversion of the Laplace transform. In this case, the first layer was taken to be finite. The ADE was also solved with a numerical finite-difference scheme, assuming a third-type condition at the inlet and a second- or third-type condition at the interface.

The solution of the ADE subject to concentration-type (first-type) inlet and interface conditions may lead to substantial mass-balance errors if the solute profile is subjected to a known solute flux. These errors are avoided by using flux- or third-type conditions, lead-

ing to a discontinuity at the soil surface and at the interface (the flux-averaged concentration, in that case, would remain continuous across the interface). A very realistic solution is obtained by requiring that both the flux and the concentration be continuous. This implies that, for the analytical solution, a first- and a third-type condition are imposed simultaneously at the interface, whereas, for the numerical solution, a second-type condition must be used at the interface. Analytical solutions for those conditions can be closely approximated by solutions for a third-type condition. Two numerical examples demonstrated that soil stratification (i.e., soil layers with different physical or chemical properties) can have major impacts on the transport of solutes in soils.

Appendix A. Numerical Integration with the Gauss-Chebyshev Formula

Numerical integration of the convolution integrals appearing in Eq. [17a] and [18a] was performed with the Gauss-Chebyshev method, which is generally more accurate at the end of the integration interval than Gaussian quadrature (Vandergraft, 1983). Also Gauss-Chebyshev offers greater flexibility in choosing the number of integration points.

The integration variable τ, varying between 0 and t, needs to be transformed into a variable η varying between -1 and $+1$. This was accomplished by the linear transformation $\tau = t(\eta + 1)/2$. For a function $f(\tau)$ the integration changes as follows:

$$\int_0^t f(\tau)\, d\tau = \frac{t}{2} \int_{-1}^{+1} f[t(\eta + 1)/2]\, d\eta \qquad [A1]$$

The Gauss-Chebyshev formula states that, for a function $g(\eta)$,

$$\int_{-1}^{+1} (1 - \eta^2)^{-1/2}\, g(\eta)d\eta = \sum_{k=1}^{n} a_k g(\eta_k) + E_T \qquad [A2]$$

where E_T is the truncation error, and η and a are the integration points and weighting coefficients, respectively:

$$\begin{aligned} \eta_j &= \cos\left(\frac{(2j-1)\pi}{2n}\right) \\ a_j &= \frac{\pi}{n} \end{aligned} \qquad j = 1,2,\ldots,n \qquad [A3]$$

where n is the number of integration points.

Using $g(\eta) = (1 - \eta^2)^{1/2} f(\eta)$, Eq. [A1] can then be evaluated according to

$$\int_0^t f(\tau)\, d\tau = \frac{\pi t}{2n} \sum_{j=1}^{n} (1 - \eta_j^2)^{1/2} f[t(\eta_j + 1)/2] \qquad [A4]$$

Appendix B. Mass Balance Calculations for the Analytical Solutions

The validity of the imposed boundary conditions and associated solutions can be evaluated by formulating a mass-balance equation in the Laplace domain, followed by analytical inversion of that equation. For $g_1 = g_2 = 0$ and $t_0 \to \infty$, assume that the solute influx is equal to the solute flux just outside the inlet boundary of the soil, and solely determined by advective transport with flowing water. Ignoring diffusion and dispersion (back diffusion) into the supply solution is realistic for most practical cases, including drip irrigation, leaching from solution reservoirs that are well

mixed, and situations involving relatively high pore-water velocities. The total solute influx, IN, across a unit cross-sectional area at $x = 0$ is then defined as

$$IN = \int_0^t \theta_1 v_1 C_o\, d\tau \qquad [B1]$$

which should be equal to the amount of solute accumulated in the profile, AC, as predicted by one of the analytical solutions

$$AC = \int_0^L R_1\theta_1 C\, dx + \int_L^\infty R_2\theta_2 C\, dx = AC_1 + AC_2 \qquad [B2]$$

A relative mass-balance error can be determined according to (see van Genuchten and Parker, 1984):

$$E_r = \frac{|AC - IN|}{IN} \times 100 \qquad [B3]$$

Equation [B2] is most easily integrated in the Laplace domain, and then inverted back into the real-time domain. The Laplace-domain solutions for first-type inlet and interface conditions, for which the solutions in the real-time domain were given by Eq. [9], [10], [16] and [17], are:

$$\overline{C}_1\ (x,s) = \frac{C_o}{s} \exp\left(\lambda_1 x\right) \qquad [B4a]$$

$$\overline{C}_2\ (x,s) = \frac{C_o}{s} \exp\left[\lambda_1 L + \lambda_2 (x - L)\right] \qquad [B4b]$$

Integration in the Laplace domain, followed by inversion of the Laplace transform, yields:

$$\begin{aligned} AC_1 = {}& \theta_1 C_o (D_1 R_1)^{1/2} \Bigg\{ (t/\pi)^{1/2} \exp(-a_1^2 t) \\ & \left[1 - \exp\left(-\frac{k^2 - 4a_1 kt}{4t}\right) \right] + \frac{1}{2a_1} \\ & + 2a_1 t - \left(\frac{1}{2a_1} + a_1 t\right) \mathrm{erfc}\,(a_1 t^{1/2}) \\ & + \frac{1}{4a_1} \exp(2a_1 k)\, \mathrm{erfc}\left(\frac{k + 2a_1 t}{2t^{1/2}}\right) \\ & - \frac{1}{4a_1}(1 - 2a_1 k + 4a_1^2 t)\, \mathrm{erfc}\left(\frac{k - 2a_1 t}{2t^{1/2}}\right) \Bigg\} \end{aligned} \qquad [B5a]$$

$$\begin{aligned} AC_2 = {}& \frac{\theta_2 C_o}{2} (D_2 R_2)^{1/2} \int_0^t \Bigg\{ \mathrm{erfc}\left[\frac{k - 2a_1 (t - \tau)}{2(t - \tau)^{1/2}}\right] \\ & + \exp(2a_1 k)\, \mathrm{erfc}\left[\frac{k + 2a_1 (t - \tau)}{2(t - \tau)^{1/2}}\right] \Bigg\} \\ & \times \left[a_2\, \mathrm{erfc}\,(-a_2 \tau^{1/2}) + \frac{\exp(-a_2^2 t)}{(\pi\tau)^{1/2}} \right] d\tau \end{aligned} \qquad [B5b]$$

where $a_k = v_k (4R_k D_k)^{-1/2}$ and $k = L(R_1/D_1)^{1/2}$. Equation [38] can be readily derived from Eq. [B3] and [B5].

For third-type conditions at the inlet and interface, the solutions in the Laplace domain are:

$$\overline{C}_1\ (x,s) = \frac{v_1}{v_1 - D_1\lambda_1} \frac{C_o}{s} \exp(\lambda_1 x) \qquad [B6a]$$

$$\overline{C}_2 (x,s) = \frac{2a_2}{a_2 + (a_2^2 + s)^{1/2}} \frac{C_o}{s}$$

$$\times \exp [\lambda_1 L + \lambda_2 (x - L)] \qquad [B6b]$$

Substitution of Eq. [B6] into Eq. [B2] and inverting gives

$$AC = \theta_1 v_1 C_o t \qquad [B7]$$

A similar approach was followed for the problem involving a finite first layer and the simultaneous use of first- and third-type conditions at the interface. However, the Laplace inversion must now be obtained numerically, since no closed-form expression in the real-time domain is available.

REFERENCES

Al-Niami, A.N.S., and K.R. Rushton. 1979. Dispersion in stratified porous media: Analytical solutions. Water Resour. Res. 15:1044–1048.

Barry, D.A., and J.C. Parker. 1987. Approximations for solute transport through porous media with flow transverse to layering. Transp. Porous Media 2:65–82.

Carslaw, H.S., and J.C. Jaeger. 1959. Conduction of heat in solids. Clarendon Press, Oxford, England.

Crump, K.S. 1976. Numerical inversion of Laplace transforms using a Fourier series approximation. J. Assoc. Comput. Mach. 23:89–96.

Dagan, G., and E. Bresler. 1985. Comment on "Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport," by J.C. Parker and M.Th. van Genuchten. Water Resour. Res. 21:1299–1300.

Danckwerts, P.V. 1953. Continuous flow systems. Chem. Eng. Sci. 2:1–13.

Jury, W.A. 1982. Simulation of solute transport using a transfer function model. Water Resour. Res. 18:363–368.

Kreft, A. 1981a. On the residence time distribution in systems with axial dispersed flow. Bull. Acad. Pol. Sci., Ser. Sci. Tech. 29:509–519.

Kreft, A. 1981b. On the boundary conditions of flow through porous media and conversion of chemical flow reactors. Bull. Acad. Pol. Sci., Ser. Sci. Tech. 29:521–529.

Kreft, A., and A. Zuber. 1978. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. Chem. Eng. Sci. 33:1471–1480.

Lapidus, L., and N.R. Amundson. 1952. Mathematics of adsorption in beds. 6. The effect of longitudinal diffusion in ion exchange and chromatographic columns. J. Phys. Chem. 56:984–988.

Leij, F.J., and J.H. Dane. 1989. Analytical and numerical solutions of the transport equation for an exchangeable solute in a layered soil. Dep. of Agronomy and Soils Ser. 139. Alabama Agric. Exp. Stn., Auburn Univ.

Lindstrom, F.T., R. Haque, V.H. Freed, and L. Boersma. 1967. Theory on the movement of some herbicides in soils: Linear diffusion and convection of chemicals in soils. J. Environ. Sci. Technol. 1:561–565.

Moranville, M.B., D.P. Kessler, and R.A. Greenkorn. 1977. Dispersion in layered porous media. AIChE J. 23:786–794.

Parker, J.C., and M.Th. van Genuchten. 1985. Reply to G. Dagan and E. Bresler. Water Resour. Res. 21:1301–1302.

Pearson, J.R.A. 1958. A note on the "Danckwerts" boundary conditions for continuous flow reactors. Chem. Eng. Sci. 10:281–284.

Selim, H.M., J.M. Davidson, and P.S.C. Rao. 1977. Transport of reactive solutes through multilayered soils. Soil Sci. Soc. Am. J. 41:3–10.

Shamir, U.Y., and D.R.F. Harleman. 1966. Numerical and analytical solutions of dispersion problems in homogeneous and layered aquifers. Tech. Rep. 89. Hydrodynamics Lab., Massachusetts Inst. of Technol., Cambridge.

Shamir, U.Y., and D.R.F. Harleman. 1967. Dispersion in layered porous media. J. Hydraul. Div. Am. Soc. Civ. Eng. 93:237–260.

Vandergraft, J.S. 1983. Introduction to numerical computations. Academic Press, New York.

van Genuchten, M.Th., and W.J. Alves. 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation. USDA Tech. Bull. no. 1661.

van Genuchten, M.Th., and J.C. Parker. 1984. Boundary conditions for displacement experiments through short laboratory soil columns. Soil Sci. Soc. Am. J. 48:703–708.

Wehner, J.F., and R.H. Wilhelm. 1956. Boundary conditions of flow reactor. Chem. Eng. Sci. 6:89–93.

Winograd, I.J. 1974. Radioactive waste storage in the arid zone. Trans. Am. Geophys. Union 55:884–894.