Boundary Conditions for Displacement Experiments through Short Laboratory Soil Columns[1]

M. Th. van Genuchten and J. C. Parker[2]

ABSTRACT

This paper presents a discussion of the physical and mathematical significance of various boundary conditions applicable to one-dimensional solute transport through relatively short laboratory soil columns. Based on mass balance considerations, it is shown that a first-type or concentration-type condition at the inlet boundary incorrectly predicts the volume-averaged or resident concentration inside both semi-infinite and finite systems. A third-type or flux-type inlet boundary condition preserves mass in semi-infinite systems, but underpredicts effluent concentrations from finite columns unless a local transformation is used to convert volume-averaged concentrations into flux-averaged concentrations. This transformation leads to an expression for the effluent concentration that is identical to the solution for the semi-infinite system using a concentration-type boundary condition. For column Peclet numbers greater than about five, the resulting analytical expression for the effluent curve is shown to be nearly identical to the analytical solution for a finite system based on a flux-type inlet boundary condition and a zero-concentration gradient at the exit boundary. Both solutions correctly preserve mass in the system; other solutions of the convective-dispersive transport equation are shown to be inappropriate for analyzing column effluent data.

Additional Index Words: dispersion coefficient, retardation factor.

PROPER formulation of boundary conditions for the analysis of column displacement experiments in the laboratory is critically important to the interpretation of observed data, as well as for subsequent extrapolation of the experimental results to transport problems in the field. Unfortunately, the most appropriate boundary conditions for a given displacement experiment are not always intuitively apparent and in many instances vastly different solutions have been applied to purportedly identical physical problems. In reducing the physical complexity of flow and transport near or across a given boundary, certain simplifying assumptions are necessary. The exact nature of these assumptions is often not immediately apparent or appreciated. As pointed out by Bear (1979), intuitively reasonable boundary conditions may lead to incongruent results, especially for relatively short soil columns. Although a few papers in the soil science literature have dealt with the effects of various boundary conditions on solute transport (e.g., van Genuchten and Wierenga, 1974; Parlange and Starr, 1975, 1978), a systematic analysis of the formulation and physical interpretation of assumed boundary conditions in re-

lation to column displacement experiments is still lacking. In this paper we will present a detailed analysis of several analytical solutions that previously have been applied to column tracer studies. Using basic principles of mass conservation, we will show that at least two of these solutions are inappropriate for analyzing column effluent data.

Recently, a number of papers in both the petroleum and chemical engineering literature have discussed in very specific terms the physical and mathematical significance of various boundary conditions (Brigham, 1974; Baker, 1977; Kreft and Zuber, 1978, 1979; Kreft, 1981; Nauman, 1981a,b; among others). In particular, these papers have pointed out the need to distinguish between volume-averaged or resident concentrations and flux-averaged or flowing concentrations. As will be discussed further in this paper, an understanding of the fundamental difference between these two concentration modes is pertinent to the selection of proper boundary conditions and associated analytical solutions. Recommendations will be given as to which set of boundary conditions are most appropriate for analyzing column effluent data.

THEORETICAL

The following partial differential equation is generally used to describe one-dimensional solute transport through a homogeneous medium during steady-state flow

$$R(\partial C_r/\partial t) = D(\partial^2 C_r/\partial x^2) - v(\partial C_r/\partial x) \qquad [1]$$

where C_r is the volume-averaged (resident) solution concentration, D is the dispersion coefficient, v is the average pore-water velocity, x is distance, and t is time. The retardation factor R is included to account for linear and reversible equilibrium adsorption. Equation [1] will be applied to finite and semi-infinite systems that are initially free of any solute:

$$C_r(x,0) = 0 . \qquad [2]$$

Analytical solution of Eq. [1] and [2] for various boundary conditions will be discussed now.

Semi-Infinite Systems

Suppose we add water from an entrance reservoir having concentration C_o to a semi-infinite profile ($0 \leqslant x < \infty$) at a rate equal to the volumetric flux $q = \theta v$, where θ is the volumetric water content of the profile. Mass conservation across the inlet boundary requires

$$[- D(\partial C_r/\partial x) + vC_r]|_{x=0^+} = vC_o \qquad [3]$$

where $x = 0^+$ indicates evaluation at the inlet boundary just inside the profile. Equation [3] is correct for a system in which the entrance reservoir physically is not connected to the column, for example, when the applied solution is slowly trickled onto the surface of the column (compare with constant rainfall). The equation is also valid for systems where the column is connected directly to the entrance reservoir, provided the assumption is made that molecular diffusion and possibly some dispersion in the fore section ($x < 0$) can be ignored. This means that the fore section is a perfectly mixed reservoir. In that case, concentrations across the inlet

boundary are macroscopically discontinuous (Danckwerts, 1953; Wehner and Wilhelm, 1956). Equation [3] specifies a Robin, third-type, or flux-type boundary condition.

For semi-infinite systems, we need an additional boundary condition specifying the behavior of $C_r(x,t)$ when $x \rightarrow \infty$. For our discussion it is sufficient to require that

$$(\partial C_r / \partial x) (\infty, t) = 0. \qquad [4]$$

The analytical solution of Eq. [1] through [4] is (e.g., see Lindstrom et al., 1967)

$$\frac{C_r(x,t)}{C_o} = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] + \left(\frac{v^2 t}{\pi DR} \right)^{1/2}$$

$$\times \exp \left[-\frac{(Rx - vt)^2}{4DRt} \right] - \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{DR} \right)$$

$$\times \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right] \qquad [5]$$

Equation [5] correctly evaluates volume-averaged or resident concentrations in semi-infinite field profiles. One may verify that [5] satisfies the mass balance requirement

$$vC_o t = R \int_0^\infty C_r(x,t) \, dx. \qquad [6]$$

In other words, whatever is added at the surface (term on the left) must be found inside the profile (term on the right).

Instead of Eq. [3], a first-type or concentration-type input boundary condition has also been used frequently:

$$C_r(0,t) = C_o. \qquad [7]$$

This equation assumes that the concentration itself can be specified at the soil surface, a situation that usually is not possible in practice. In essence, Eq. [7] indicates that the concentration is continuous across the inlet boundary. While the stipulation of such a concentration continuity at $x = 0$ may have an intuitive appeal, it is obtained at the cost of maintaining a solute flux continuity across the inlet position. Consequently, Eq. [7] is incorrect for displacement experiments where the tracer solution is added at a specified rate. This becomes evident when considering the analytical solution of Eq. [1], [2], [4] and [7] (Lapidus and Amundson, 1952):

$$\frac{C_r(x,t)}{C_o} = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right]$$

$$+ \frac{1}{2} \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right]. \qquad [8]$$

Substitution of this equation into Eq. [6] shows that the mass balance identity is not satisfied. If we define a relative error E as (see also Eq. [6])

$$E = (1/vC_o t) [R \int_0^\infty C_r(x,t) \, dx - vC_o t] \qquad [9]$$

then, upon integration, it is easily shown that for Eq. [8]

$$E(\zeta) = \frac{1}{(\pi \zeta)^{1/2}} \exp \left(-\frac{\zeta}{4} \right) + \frac{1}{\zeta}$$

$$- \left(\frac{1}{2} + \frac{1}{\zeta} \right) \operatorname{erfc} \left(\frac{1}{2} \sqrt{\zeta} \right) \qquad [10]$$

where

$$\zeta = v^2 t / DR. \qquad [11]$$

Equation [10] can be derived also by considering the actual solute flux density J_s into the column at $x = 0$:

$$J_s(0,t) = \left[qC_o - \theta D (\partial C_r / \partial x) \right] |_{x=0^+}. \qquad [12]$$

This equation indicates that in addition to the convective mass flux qC_o, a dispersive component is operative at the boundary. This dispersion term is responsible for the observed mass balance deviations, as can be shown by defining the relative error E in terms of J_s:

$$E = \frac{1}{qC_o t} \left[\int_0^t J_s(0,\tau) \, d\tau - qC_o t \right]$$

$$= -\frac{D}{vC_o t} \int_0^t \frac{\partial C_r(x,\tau)}{\partial x} \, dt \bigg|_{x=0}. \qquad [13]$$

Substituting Eq. [8] into Eq. [13] also leads to Eq. [10]. Figure 1 shows that the relative error in the mass balance can be extremely large for small values of the dimensionless parameter ζ, i.e., at early times, for systems where dispersive transport is large compared to convective transport, and for systems where the solute is strongly adsorbed by the solid phase (large R). Hence, concentration-type boundary condition Eq. [2] fails to satisfy conservation of mass and the discrepancy is not always negligible.

Finite Systems

The challenge here is to define a boundary condition that describes as realistically as possible the physical process of flow and transport across the exit boundary of a finite system. One requirement that always must be satisfied is continuity of the solute velocity across the lower boundary:

$$\left[-D (\partial C_r / \partial x) + vC_r \right]_{x=L^-} = vC_e \qquad [14]$$

where L^- indicates evaluation just inside the column, and where $C_e = C_e(t)$ is the exit concentration. As with Eq. [3] for the inlet boundary, Eq. [14] assumes that diffusion-dispersion phenomena in the exit reservoir are negligible, or that the exit reservoir is not in direct physical contact with the liquid phase inside the column. This last situation may occur when the effluent solution drips freely from the exit boundary (e.g., see the fraction collector system described by Wierenga et al., 1975).

Because of the addition of an extra unknown (C_e), Eq. [14] leads to an indeterminate system of equations. Hence, an additional equation is needed to fully describe the system. One such equation is based on the intuitive assumption that the solute concentration should be continuous across the lower boundary:
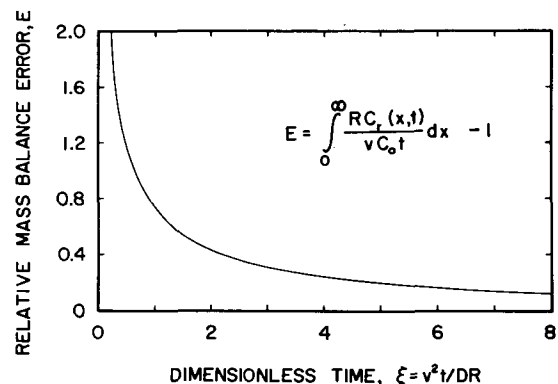
$$C_r(L^-,t) = C_e(t). \qquad [15]$$

Fig. 1—Plot of the relative mass balance error, E, vs. dimensionless time ζ for analytical solution [8].

Substitution of this equation into [14] leads to the frequently used boundary condition

$$(\partial C_r / \partial x)\,(L, t) = 0 . \qquad [16]$$

It is important to realize that Eq. [16] is based on an assumption, namely that the concentration macroscopically should be continuous at $x = L$ (Danckwerts, 1953; Wehner and Wilhelm, 1956, Pearson, 1959). It is difficult to reason a priori whether this assumption is reasonable in view of the uncertainty of the exact physical processes at or near the lower boundary. However, the requirement of a continuous distribution at $x = L$ seems inconsistent with Eq. [3] for the inlet boundary which not only results in a discontinuous distribution at $x = 0$, but also in a nonzero concentration gradient at the column entrance.

Nevertheless, if we accept Eq. [16] as an appropriate boundary condition for finite columns, then the physical system is completely defined and can be solved. The analytical solution of Eq. [1], [2], [3] and [16] is (Brenner, 1962)

$$\frac{C_r(x, t)}{C_o} = 1 -$$

$$\sum_{m=1}^{\infty} \frac{\dfrac{2vL}{D}\,\beta_m \left[\beta_m \cos\!\left(\dfrac{\beta_m x}{L} \right) + \dfrac{vL}{2D}\sin\!\left(\dfrac{\beta_m x}{L} \right) \right]}{\left[\beta_m^2 + \left(\dfrac{vL}{2D} \right)^2 + \dfrac{vL}{D} \right]\left[\beta_m^2 + \left(\dfrac{vL}{2D} \right)^2 \right]}$$

$$\times \exp\!\left(\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m Dt}{L^2 R} \right) \qquad [17]$$

where the eigenvalues β_m are the positive roots of

$$\beta_m \cot(\beta_m) - (\beta_m^2 D / vL) + (vL/4D) = 0 . \qquad [18]$$

If applied to effluent curves ($x = L$) and using dimensionless variables, the solution simplifies to

$$\frac{C_e(T)}{C_o} = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin(\beta_m)\exp\!\left(\dfrac{P}{2} - \dfrac{PT}{4R} - \dfrac{\beta_m^2 T}{PR} \right)}{\beta_m^2 + \dfrac{P^2}{4} + P}$$

$$[19]$$

$$P\beta_m \cot(\beta_m) - \beta_m^2 + \frac{P^2}{4} = 0 \qquad [20]$$

$$T = vt/L \qquad P = vL/D \qquad [21]$$

where T is the number of pore volumes leached through the column, and P is the column Peclet number. Computational programs for evaluating Brenner's series solution are readily available (van Genuchten and Alves, 1982). The series solution converges only for relatively small values of P. For large P-values, computationally efficient and very accurate approximate solutions have also been obtained.

Analogous to Eq. [6] for semi-infinite systems, the mass balance requirement for finite columns is

$$v \int_0^t \left[C_o - C_e(\tau) \right] d\tau = R \int_0^L C_r(x, t)\,dx . \qquad [22]$$

This equation states that whatever is added to the column minus what is leaving the column (left side) must be stored in that column (right side). Upon substitution, it is readily shown that Brenner's solution satisfies [22].

We have emphasized that Brenner's solution for C_e satisfies Eq. [3] for the inlet boundary, Eq. [14] for the outlet boundary, and that the requisite system of equations is completed by assuming that $C_e(t) = C_r(L, t)$. An alternative way of completing the system of equations is to assume that solute distributions inside the finite column are unaffected by

the presence of an outflow boundary or effluent collection system, thus considering the column to be part of an effectively semi-infinite system. The requisite additional stipulation that $\partial C_r(\infty, t)/\partial x = 0$ may then be invoked, which in turn suggests that Eq. [5] adequately describes the concentration distribution *within* the column. However, solution [5] does not immediately predict the effluent concentration since we have no longer imposed Brenner's assumption that $C_e(t) = C_r(L, t)$. An expression for the effluent concentration can nevertheless be obtained by substitution of Eq. [5] directly into Eq. [14] which yields

$$\frac{C_e(t)}{C_o} = \frac{1}{2}\,\mathrm{erfc}\!\left[\frac{RL - vt}{2(DRt)^{1/2}} \right]$$

$$+ \frac{1}{2}\exp(vL/D)\,\mathrm{erfc}\!\left[\frac{RL + vt}{2(DRt)^{1/2}} \right] \qquad [23]$$

or in dimensionless form

$$C_e(T)/C_o = \frac{1}{2}\,\mathrm{erfc}\!\left[(P/4RT)^{1/2}(R - T) \right]$$

$$+ \frac{1}{2}\exp(P)\,\mathrm{erfc}\!\left[(P/4RT)^{1/2}(R + T) \right] \qquad [24]$$

Note that Eq. [23] is *exactly* the same as Eq. [8] when evaluated at $x = L$. Equation [23] can be derived also by considering C_e to be the unknown closing term of mass balance Eq. [22]. Differentiating that equation with respect to time and solving for the effluent concentration gives

$$C_e(t) = C_o - \frac{R}{v}\int_0^L \frac{\partial C_r(x, t)}{\partial t}\,dx . \qquad [25]$$

In other words, the effluent concentration equals the input concentration minus the change in the amount of solute stored in the column. Substituting Eq. [5] into Eq. [25] and carrying out the indicated integration leads directly to Eq. [23]. A third equivalent expression for $C_e(t)$ is given by

$$C_e(t) = \frac{R}{v}\int_L^\infty \frac{\partial C_r(x, t)}{\partial t}\,dx \qquad [26]$$

which states that the effluent concentration equals the time derivative of the amount of solute that would be stored in the region $L < x < \infty$ if the column were to be part of a semi-infinite system. Equation [26] can be obtained by taking the time derivative of Eq. [6] and using the resulting expression to eliminate C_o from Eq. [25].

The analysis above indicates that the flux-type inlet boundary condition in Eq. [3] properly conserves mass when used to calculate volume-averaged or resident concentration distributions in semi-infinite systems. The analytical solution for this problem (Eq. 5) can be used also to derive an expression for the breakthrough curve, $C_e(t)$, from a finite column; the expression turns out to be identical to the analytical solution for a first-type input boundary condition and a semi-infinite system (Eq. 23). This relationship between the two semi-infinite solutions has been described previously (Brigham, 1974; Kreft and Zuber, 1978; Parker and van Genuchten, 1984; among others). It is a direct consequence of a transformation similar to [14] but applicable at any given distance, x. This transformation will be discussed next.

Flux-Averaged vs. Volume-Averaged Concentrations

Equation [1] is written in terms of the in-situ, volume-averaged, or resident concentration, C_r, which is the mass of solute per unit volume of fluid contained in an elementary volume of the system at a given instance. One can also define a flux-averaged or flowing concentration, C_f, which is the mass of solute per unit volume of fluid passing through

a given cross-section during an elementary time interval (Kreft and Zuber, 1978):

$$C_f = C_r - (D/v)(\partial C_r/\partial x) \qquad [27]$$

Substitution of Eq. [27] into Eq. [1] leads to exactly the same transport equation, except that the resident concentration C_r is replaced by the flux concentration, C_f:

$$R(\partial C_f/\partial t) = D(\partial^2 C_f/\partial x^2) - v(\partial C_f/\partial x). \qquad [28]$$

Hence, spatial and temporal distributions of C_r and C_f are described by the same governing equation. Boundary condition [4] also holds for both C_r and C_f; this follows immediately by noting that the second spatial derivative of [5] vanishes when $x \to \infty$. Finally, application of Eq. [27] to boundary condition [3] leads to

$$C_f(0,t) = C_o. \qquad [29]$$

Hence, transport equations that describe resident concentrations in semi-infinite systems subject to first-type inlet boundary conditions are mathematically identical to transport equations that describe flux concentrations in semi-infinite systems subject to first-type inlet boundary conditions. This observation shows that the solution of Lapidus and Amundson, given by Eq. [8], predicts flux concentrations in a semi-infinite system, and if extended to a finite column, properly describes the effluent concentration.

Equation [27] can be applied also to Brenner's solution for a finite system. Substituting Eq. [17] into Eq. [27] yields the following expression for the flux concentration C_f

$$\frac{C_f(x,t)}{C_o} = 1 -$$

$$\sum_{m=1}^{\infty} \frac{2\beta_m \sin\left(\frac{\beta_m x}{L}\right)\exp\left(\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m^2 Dt}{L^2 R}\right)}{\beta_m^2 + \left(\frac{vL}{2D}\right)^2 + \frac{vL}{D}}$$

$$[30]$$

where the eigenvalues β_m are the same as before (Eq. 18). Note that Eq. [30] at the exit boundary $x = L$ is the same as Eq. [19]. This follows also immediately from Eq. [27] and boundary condition [16]. Hence, flux and resident concentrations as calculated with Brenner's solution are identical at the exit boundary. However, they can be quite different inside the column. This is shown in Fig. 2 where the two concentration modes are plotted versus reduced distance (x/L) using a value of 5 for P. Figure 2 also shows the solution of Cleary and Adrian (1973) for boundary conditions [7] and [16], i.e. (see also van Genuchten and Alves, 1982),
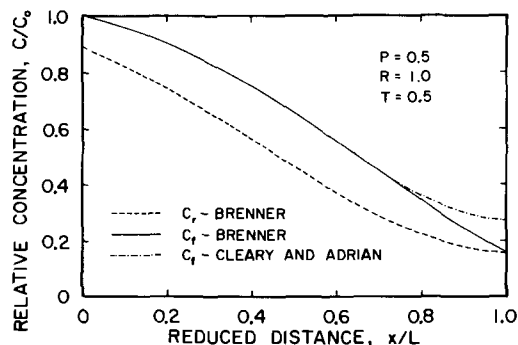
Fig. 2—Distributions vs. reduced distance of relative volume-averaged and flux-averaged concentrations predicted with Brenner's solution, and relative flux-averaged concentrations predicted with the solution of Cleary and Adrian.

$$\frac{C_f(x,t)}{C_o} = 1 -$$

$$\sum_{m=1}^{\infty} \frac{2\alpha_m \sin\left(\frac{\alpha_m x}{L}\right)\exp\left(\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\alpha_m^2 Dt}{L^2 R}\right)}{\alpha_m^2 + \left(\frac{vL}{2D}\right)^2 + \frac{vL}{2D}}$$

where the α_m are the positive roots of $\qquad [31]$

$$\alpha_m \cot(\alpha_m) + (vL/2D) = 0. \qquad [32]$$

Note that we ostensibly assumed that Cleary and Adrian's solution represents flux concentrations rather than resident concentrations. Because of boundary condition [16], $C_r(L,t) = C_f(L,t) = C_e(t)$ for Cleary and Adrian's solution, as was the case for Brenner's solution.

Figure 2 shows that the solution of Cleary and Adrian (1973) deviates substantially from the flux concentration (Eq. [30]) as derived from the solution of Brenner (1962). This deviation is caused by the fact that boundary condition [16] is not invariant by the transformation from C_r to C_f (the second spatial derivative at $x = L$ is not zero). Thus, if Brenner's solution is taken as the correct expression for the resident concentration, then Cleary and Adrian's solution leads to an incorrect description of the flux concentration. Alternatively, one may also argue that if Cleary and Adrian's solution were to represent flux concentrations, then Brenner's solution cannot represent resident concentrations. This inconsistency gives additional support to our contention that Eq. [16] is based on a convenient but purely intuitive assumption.

DISCUSSION

To appreciate the differences between various analytical solutions that are potentially applicable to column displacement experiments, Fig. 3 shows calcu-
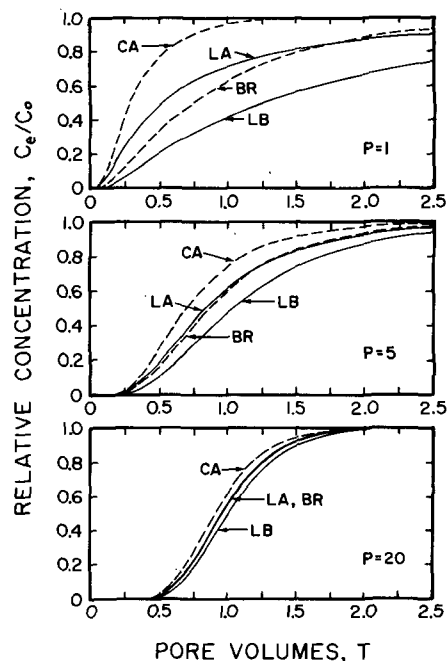
Fig. 3—Relative effluent concentration profiles for analytical solutions CA (Cleary and Adrian, 1973), LA (Lapidus and Amundson, 1952), LB (Lindstrom et al., 1967) and BR (Brenner, 1962). The effluent curves are plotted for three values of the column Peclet number, P.

lated effluent curves for three values of the column Peclet number, P. Plotted are the solutions of Cleary and Adrian (1972), Lapidus and Amundson (1952), Lindstrom et al. (1967), and Brenner (1962), referred to respectively by CA, LA, LB, and BR and given in this same order by Eq. [31], [8], [5], and [17]. Note that the four solutions deviate drastically when $P = 1$, but slowly converge to each other as P increases. Analytical solutions LA and BR are very similar when $P = 5$, while essentially no differences between these two solutions are present when P reaches a value of 20.

An important attribute of a breakthrough curve from a finite column is the area above each curve. This area, sometimes referred to as the holdup (H), should represent the amount of solute that can be stored in the column. Mathematically, H is given by

$$H = \int_0^\infty [1 - C_e(T)/C_o] \, dT. \qquad [33]$$

One may verify that $H = R$ for the two curves designated LA and BR in Fig. 3. For the curve CA (Eq. [31]), H is given by

$$H = R[1 - (1/P) - (e^{-P}/P)] \qquad [34]$$

while for curve LB (Eq. [5])

$$H = R[1 + (1/P)]. \qquad [35]$$

Figure 4 gives a plot of the relative holdup (H/R) vs. P for the four analytical solutions for $C_e(T)$. Note that H/R deviates substantially from 1.0 for the solutions of Cleary and Adrian (1972) and Lindstrom et al. (1967). These deviations illustrate that highly inaccurate estimates for R can be obtained when the solutions CA or LB are fitted to observed effluent data, especially when P is small. For example, analytical solution LB overestimates R by no less than 50% when $P = 2$.

The solutions LA and BR always lead to correct estimates for R, independently of the value of the Peclet number. However, the two solutions may yield somewhat different estimates of P, especially when P becomes less than about 5 (Fig. 3). As discussed earlier, LA and BR each are based on different assumptions regarding the physics of flow and transport at or near the lower boundary. Because of the apparent inconsistency in the stipulation of finite and zero concentration gradients at the inlet and outlet boundaries for Brenner's solution, and because of its numerically more tedious form compared to Eq. [8], we recom-
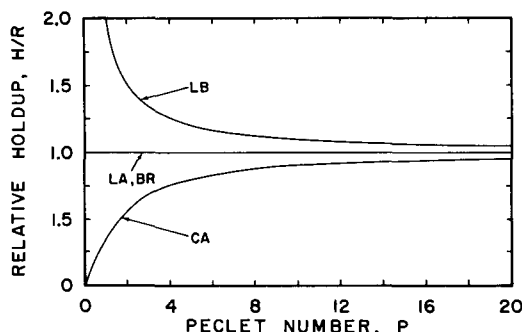
mend that only the solution of Lapidus and Amundson (1952) be used to calculate effluent curves from finite columns. Of course, this same solution (Eq. [8]) should also be used to calculate solute fluxes in the field. Similarly, we recommend that only the solution of Lindstrom et al. (1967) be used to evaluate in situ, volume-averaged concentrations.

In some cases, breakthrough curves are obtained within laboratory columns by means of suction cups or other extraction devices. In that case, it is difficult to reason which concentration mode will be observed. Because the extracted soil solution is obtained at a fixed location in the soil, it is unlikely that the observed data are flux concentrations. However, because of the transient behavior of displacement experiments and the uncertainty of how exactly flow lines are disrupted by the installation and performance of suction cups, the observed concentration mode is probably not exactly that of a resident concentration either. This problem is pertinent for both laboratory and in situ field measurements.

It should be noted that transformation [27] from resident to flux concentrations has been shown to hold only for Eq. [1] and its analytical solutions for a semi-infinite system (LB and LA). The transformation may not necessarily hold for more complicated transport models (e.g., for certain kinetic adsorption models). In that case, flux concentrations—and hence breakthrough curves—are best calculated by first deriving the analytical solution for the resident concentration and subsequently applying Eq. [14] to obtain an expression for the effluent curve.

SUMMARY AND CONCLUSIONS

This study shows that solute transport in a semi-infinite field profile is described properly with analytical solution [5] for a flux-type soil surface input boundary condition. The analytical solution for this problem can be used also to describe resident (volume-averaged) solute distributions inside finite soil columns. However, the solution needs to be modified if applied to effluent curves from finite columns. Based on mass balance calculations, and assuming that the column exit boundary does not alter flow lines upstream of the boundary, an equation for the breakthrough curve (Eq. [23]) can be derived that is mathematically similar to the solution for a concentration-type soil surface inlet boundary condition. This similarity is not accidential but results from a transformation from volume-averaged (C_r) to flux-averaged (C_f) concentrations. A similar transformation fails for two available solutions applicable to finite systems.

Of the two solutions for a finite system, only the solution of Brenner (1962) for the flux-type inlet boundary condition conserves mass in the system. This solution leads to an expression for the effluent curve that is nearly identical to the derived expression [23] for the breakthrough curve from a finite profile, provided the column Peclet number is not much less than about 5.

Because of some inconsistencies in the stipulation of concentration continuities at the inlet and outlet boundaries for Brenner's solution and because of its numerically more tedious form compared to the so-

Fig. 4—Relative holdup (H/R) vs. column Peclet number, P, for analytical solutions CA, LA, LB and BR.

lution of Lapidus and Amundson (1952), we recommend that the latter solution always be used to evaluate flux-averaged concentrations, whether they pertain to finite systems (effluent curves) or semi-infinite field profiles. We similarly recommend that only the solution of Lindstrom et al. (1967) be used for volume-averaged concentrations.

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