

COMMENTS AND LETTERS TO THE EDITOR

Comments on "Boundary Conditions for Displacement Experiments Through Short Laboratory Soil Columns"

In a recent paper van Genuchten and Parker (1984) discussed various boundary conditions which have been used in miscible displacement studies. Although we agree with most of their points, we believe that they overemphasized the shortcomings of Brenner's solution (Brenner, 1962) which was obtained following Danckwerts' (1953) prescription for boundary conditions. At the inlet boundary the condition is

$$-D(\partial Cr/\partial x) + vCr = vC_0, x = 0, t > 0. \quad [1]$$

Except for limiting cases, Eq. [1] will normally yield $Cr \neq C_0$, leading to an apparent discontinuity in concentration at the inlet, i.e., between the soil column and the inlet reservoir. The authors use this as an argument to justify a possible discontinuity at the outlet. We shall show that it is physically possible to have a discontinuity in concentration at the inlet but not at the outlet of the column. Consider the steady state flow

$$v dCr/dx = D d^2Cr/dx^2, \quad [2]$$

which applies within the column. Eq. [2] has the solution

$$Cr = A + B \exp[-(L-x)v/D] \quad [3]$$

where L is some distance and A and B are constants. The exponential term is vanishingly small for $x < L$ and increasingly large for $x > L$, as long as the corresponding Péclet numbers are large. An increasingly large term is not physical, thus $B = 0$ for $x > L$. A rapid variation in Cr is possible for $x < L$ but not for $x > L$. Parlange and Starr (1975) utilized such a boundary layer for $x < L$ to accommodate the boundary condition (Danckwerts, 1953),

$$\partial Cr/\partial x = 0 \text{ at } x = L \quad [4]$$

where L then stands for the column length. In general, a boundary layer is possible *upstream* from a given position but not *downstream*. When a reservoir is in contact with the column inlet ($x = 0$) a boundary layer will form for $x < 0$, i.e., the concentration can vary rapidly for $x < 0$ in the reservoir from $Cr(x = 0)$ to C_0 . In that case D may stand for the molecular diffusion, D_0 , with $D_0 \ll D$ in the column, as long as the flow in the reservoir is laminar, i.e., if it is *not* well mixed. Thus when D_0 is considered negligible, the thickness of the boundary layer is infinitely thin and an apparent, or macroscopic, discontinuity between C_0 and Cr is sustainable at $x = 0$.

In contrast, at the column outlet ($x > 0$) no boundary layer can develop so there must be continuity in concentration at $x = L$. For nonsteady state conditions a growing boundary layer must be considered but this does not affect its existence, which is all that concerns us here (cf. Wehner and Wilhelm, 1956). If there is continuity at the outlet then Eq. [4] holds although van Genuchten and Parker (1984) observe that there is often some uncertainty of the exact physical processes at the outlet. The argument here is not about this real difficulty but in pointing out that the analysis of the boundary layers near the inlet and outlet show no inconsistency between the derivations of Eq. [1] and [4].

van Genuchten and Parker (1984) conclude that the solution of the transport equation using Eq. [1] and assuming a semi-infinite column is fundamental to predict the profile for *all* Péclet numbers because they "assume that solute distributions inside the finite column are unaffected by the presence of an outflow boundary". We believe that the experimental conditions necessary for the assumption to hold

may be hard to implement. Rather for $vLD > 4$ any outlet condition, which will normally be given by Eq. [4], corrects the profile upstream for a short distance only and the correction can usually be obtained readily using boundary layer theory (Parlange and Starr, 1975, 1978). We have also shown that when Eq. [1] and [4] hold, and for $vL/D > 4$, an appropriate breakthrough curve is often obtained by considering a semi-infinite column and taking $Cr = C_0$, at the inlet (Parlange and Starr, 1975, 1978). Our point of departure with van Genuchten and Parker (1984) is that we believe that the simpler solutions can be used safely only for Péclet numbers larger than four, which is the usual case for most practical situations.

Finally physical uncertainties may affect not only the boundary condition at the outlet, Eq. [4], but also at the inlet, Eq. [1]. The latter presumes that the flow is perfectly one-dimensional, which is not necessarily the case. For instance Starr and Parlange (1976) considered a case when a stagnant phase develops at the inlet and Eq. [1] does not hold there. In that case and more generally when the solute moves in two different phases, e.g., one rather mobile and one rather stagnant, not only the boundary conditions may be affected but also the transport equation. That is, it is dangerous to assume a priori that a single transport equation can be used to describe the flow if two phases are present. Rather, an equation for each phase must then be considered.

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Griffith University,
Brisbane, Queensland, 4111
Australia

J.-Y. PARLANGE
D. A. BARRY

USDA-ARS-BARC
Beltsville, MD 20705

J.L. STARR

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Reply to "Comments on Boundary Conditions for Displacement Experiments Through Short Laboratory Soil Columns"

Parlange et al. in essence comment on three issues: 1. our overemphasis in their view of the shortcomings in Brenner's solution, 2. the need to restrict column displacement experiments to Péclet numbers greater than about four, and 3. the effects of physical disturbances due to imperfect inlet and outlet boundaries. We wish to reply to their comments. For convenience we use the same abbreviations for the 4 analytical solutions as in our paper (van Genuchten and Parker, 1984): BR for the solution of Brenner (1962), CA for the solution of Cleary and Adrian (1973), LA for the solution of Lapidus and Amundson (1952), and LB for the solution of Lindstrom et al. (1967).

1. We indeed raised questions regarding the applicability of Brenner's solution BR to transport through a finite system. Brenner's solution imposes a third-type boundary condition at $x = 0$ and a zero-gradient condition at the column exit, $x = L$. The last condition is based on the *intuitive assumption* (e.g., see Wehner and Wilhelm, 1956) that concentrations should be continuous across the exit boundary. While this requirement certainly must be met at the *microscopic* level, continuity of concentration does not necessarily follow at the *macroscopic* level when discontinuities in medium properties are imposed. The analysis by Parlange et al. (like the more general discussion by Wehner and Wilhelm, 1956) has not convinced us otherwise. In our opinion, continuity cannot be deduced from the observation that no physical boundary layer will develop in the exit reservoir $x > L$. Even if a zero gradient is present outside the column, it tells nothing about the mathematical boundary layer associated with a discontinuity in medium properties. Macroscopically and from an analytical perspective, it is convenient to consider an infinitesimally thick boundary region within which the dispersion coefficient and porosity change from porous medium to bulk solution values. Imposing discontinuities in these parameters must yield a macroscopic concentration discontinuity. The dilemma of flux vs. concentration discontinuity at porous media boundaries can be avoided by not imposing the infinitesimal boundary region assumption. As the window of an averaging volume glides through the boundary region, hypothetical discontinuities in medium properties will be smoothed and macroscopic concentrations as well as fluxes become continuous. Inasmuch as boundaries are mathematical approximations of reality, it is also important to consider the physical implications of invoked simplifications. For example, combining diffusion and hydrodynamic dispersion in a single coefficient can lead to difficulties since diffusive transport may occur in both upstream and downstream directions at boundaries that are continuous with a fluid phase, while hydrodynamic dispersion will be constrained to the downstream direction. Finally, we note that Brenner's solution specifies volume-averaged concentrations C_r . As we discussed in our paper and elsewhere (Parker and van Genuchten, 1984), alternative solutions can be obtained when the transport equation is expressed in terms of the flux-averaged concentration C_f , which is related to C_r by

$$C_f = C_r - (D/v) (\partial C_r / \partial x) \quad [1]$$

Using a first-type inlet boundary condition and again a zero-gradient at $x = L$, solution CA results. As shown in our Fig. 2, this solution differs from the flux-concentration that can be derived indirectly from BR upon application of Eq. [1] above. This inconsistency may reflect inherent weaknesses in the either CA and/or BR, although we tend to believe that CA is at fault because of its failure to preserve mass (see our Fig. 4). Nevertheless, the discussion above shows some perils in Brenner's solutions that are not easily solved. As a more plausible alternative to Brenner's approach, we suggest to regard concentrations inside the column to be unaffected by the exit boundary; this allows us to use solutions for a semi-infinite system, notably LA for flux-averaged and LB for volume-averaged concentrations. Contrary to CA and BR, these two solutions *are* properly related through transformation [1] above. Thus, LA correctly preserves mass when integrated vs. time at any point in the profile (or effluent), while LB always preserves mass when integrated versus depth.

2. From the discussion above and our Fig. 4, it follows that both LA and BR correctly predict the retardation factor R in the system, and hence that both solutions *can* be used safely to derive adsorption or exchange coefficients from column displacement experiments (as opposed to batch equilibration). This conclusion is valid independently of the value of P . However, we do acknowledge that application of BR

and LA will lead to different dispersion coefficients (or Péclet numbers) when short laboratory columns are used (notably when P is less than about 5; see our Fig. 3). Fortunately, this last issue is mostly academic since dispersion coefficients measured from laboratory columns are generally non-representative of the field scale anyway. The problem of mass conservation nevertheless remains important. Column displacement experiments are often used to study the transport of heavy metals, radionuclides, or other strongly adsorbed solutes. Because of large retardation factors, any practical study must be limited to relatively small soil columns. Our study shows that LA and BR can be used safely to measure R , irrespective of the P -value. Contrary to the suggestion by Parlange et al., this conclusion holds also for $P < 4$ provided the exact series solution of BR is used. Mass conservation may become a problem when approximate solutions (Brenner, 1962; Parlange and Starr, 1975) are used at relatively small P -values. These approximations were derived because available series solutions were found to diverge for large P -values. Use of the approximate solutions hence should be restricted to the larger P -values. Because the series solutions converge rapidly for P -values less than about 20, and because computationally efficient algorithms are available (van Genuchten and Alves, 1982), we also see no need to extrapolate the approximate solutions to P -values for which they are known to be inaccurate.

3. Finally, we agree with Parlange et al. that physical disturbances at or near the inlet and exit boundaries may affect the value of the measured dispersion coefficient. However, one should still be able to correctly measure the retardation factor provided (i) the inlet or outlet screens/porous plates are chemically inert and do not hold water, and (ii) retardation factors are measured by fitting theoretical curves to the entire effluent curve and not just to a limited portion of the curve (notably the initial breakthrough part or to that part of the curve where the relative concentration is approximately 0.5). In instances where severe tailing of breakthrough curves is observed, the use of two-region ("mobile-immobile" type) models may be required.

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U.S. Salinity Laboratory M. TH. VAN GENUCHTEN
4500 Glenwood Drive
Riverside, CA 92501

Dep. of Agronomy J. C. PARKER
Virginia Polytechnic Inst.
and State Univ.
Blacksburg, VA 24061

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