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COMMENTS & LETTERS TO THE EDITOR

Reprinted from
Soil Science Society of America Journal
Vol. 58, No. 3, May-June 1994.

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

We appreciate the comment by Shukla on our 1984 study (van Genuchten and Parker, 1984) dealing with the use of suitable boundary conditions for column displacement experiments. Shukla's comment focuses on the correctness of a solute mass balance equation we applied to the column during a given tracer experiment. Although not specifically mentioned in his comment, the underlying issue of Shukla's and our analysis is selection of the most appropriate inlet boundary condition for solute transport experiments. We hope that the derivation below will convince Shukla of the correctness of our previous analysis.

Let us first restate the two conditions usually applied to the inlet boundary of a column (or, for that matter, the soil surface in the case of field tracer experiments). These conditions are a third-type (or fiux-type) boundary condition, which assumes solute flux continuity across the inlet boundary:

$$\left(-D\frac{\partial C_r}{\partial x} + vC_r\right)\Big|_{x=0+} = vC_o \quad [1]$$

and a first-type (Dirichlet, or concentration-type) condition, which assumes concentration continuity:

$$C_r(0+,t) = C_o \quad \mathbf{[2]}$$

where C_r is the volume-averaged (resident) concentration, C_o is the concentration of the applied solution, D is the dispersion coefficient, v the pore-water velocity, x is distance, t is time, and $x = 0+$ indicates evaluation just inside the column. Restricting ourselves to semi-infinite systems ($0 \leq x \leq \infty$), we also give a general equation for the relative mass balance error, E, for a column displacement experiment involving any assumed inlet condition:

$$E(t) = \frac{1}{I_s(t)}\left[\theta R\int_0^\infty C_r(x,t)\mathrm{d}x - I_s(t)\right] \quad [3]$$

where θ is the volumetric water content, R is the solute retardation factor, and I_s is the cumulative solute flux entering the soil column across the inlet boundary at $x = 0$:

$$I_s(t) = \int_0^\infty J_s(x,t)\mathrm{d}x|_{x=0+} \quad [4]$$

in which $J_s(x,t)$ is the solute flux density at any x and t in the medium:

$$J_s(x,t) = -\theta D\frac{\partial C_r}{\partial x} + \theta vC_r \quad [5]$$

In van Genuchten and Parker (1984) we discussed why in most cases boundary condition Eq. [1] should be used for solute transport experiments. This condition specifies a given solute flux density. The equation is valid as long as *diffusion* across the inlet boundary is small relative to convective transport by flowing water. By contrast, Eq. [2] assumes that somehow the concentration at the inlet boundary can be made equal to C_o, irrespective of any diffusion or dispersion process in the foresection or inside the soil column. The case of a purely diffusive system (v = 0) is not described correctly by either Eq. [1] or [2]. A more appropriate analysis for this limiting case would be to explicitly consider solute transport in both the foresection and the soil column using a two-layer medium approach (e.g., as was done by Wehner and Wilhelm [1956] for convective-dispersive transport), or to invoke an approximate mixed condition often used in heat transfer and chemical diffusion studies (e.g., Bird et al., 1960):

$$\frac{\partial C_r}{\partial x}(0+,t) = \frac{k}{D}\left[C_o - C_r(0+,t)\right] \quad [6]$$

where k is a mass transfer coefficient.

We maintain, as in our 1984 study, that Eq. [1] is the most appropriate boundary condition for most or all solute displacement experiments. Given this selection, the mathematical analysis is straightforward. The solute flux $J_s(0+,t)$ for a third-type inlet condition follows immediately from Eq. [1] and [5] as

$$J_s(0+,t) = \theta vC_o \quad [7]$$

and Eq. [3] reduces to our previous Eq. [9], i.e.,

$$E(t) = \frac{1}{vC_o t}\left[R\int_0^\infty C_r(x,t)\mathrm{d}x - vC_o t\right] \quad [8]$$

Substituting the analytical solution for a third-type inlet condition (Lindstrom et al., 1967) into Eq. [8] gives, as expected, a zero mass-balance error. However, if analytical solution LA of Lapidus and Amundson (1952) is incorrectly used in Eq. [3], E can become quite large, as indicated by Fig. 1 of van Genuchten and Parker (1984). We conclude that our previous analysis was correct, and nothing in our 1984 study should be corrected or modified (including our previous Eq. [9] and [10], as well as Fig. 1).

Although somewhat irrelevant, one can go through a similar mass-balance analysis as was done above for Eq. [1], when boundary condition Eq. [2] is somehow forced to be valid. Substituting the LA solution for a first-type condition in Eq. [5] leads then to

$$J_s(x,t) = \theta C_o\left\{\left[\frac{DR}{\pi t}\right]^{1/2}\exp\left[-\frac{(Rx-vt)^2}{4DRt}\right] + \frac{v}{2}\mathrm{erfc}\left[\frac{Rx-vt}{2\sqrt{DRt}}\right]\right\} \quad [9]$$

which for x = 0+ reduces to

$$J_s(0+,t) = \theta C_o\left[\left[\frac{DR}{\pi t}\right]^{1/2}\exp\left[-\frac{v^2t}{4DR}\right] + \frac{v}{2} + \frac{v}{2}\mathrm{erf}\left[\frac{v\sqrt{t}}{2\sqrt{DR}}\right]\right] \quad [10]$$

Note that this equation deviates from Shukla's Eq. [11. Integration of Eq. [10] from 0 to t gives finally

$$I_s(t) = \theta C_o\left[\left[\frac{DRt}{\pi}\right]^{1/2}\exp\left[-\frac{v^2t}{4DR}\right] + \frac{DR}{v} + vt - \left[\frac{vt}{2} + \frac{DR}{v}\right]\mathrm{erfc}\left[\frac{v\sqrt{t}}{2\sqrt{DR}}\right]\right] \quad [11]$$

One may verify that no mass-balance errors occur *(E = 0)* when Eq. [1 1] and the LA solution are substituted in Eq. [3]. This result is not surprising since any solution of the convection-dispersion equation should conserve mass when considered inside the column. Again, the real challenge is correctly defining the solute flux, $J_s(0-,t)$, entering the soil column; in most or all situations this flux is given as implied by the right-hand side of Eq. [1], i.e., $J_s(0-,t) = \theta vC_o$.

Received 31 Dec. 1993.

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