

Flux-Averaged and Volume-Averaged Concentrations in Continuum Approaches to Solute Transport

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Transformations between volume-averaged pore fluid concentrations and flux-averaged concentrations are presented which show that both modes of concentration obey convective-dispersive transport equations of identical mathematical form for nonreactive solutes. The pertinent boundary conditions for the two modes, however, do not transform identically. Solutions of the convection-dispersion equation for a semi-infinite system during steady flow subject to a first-type inlet boundary condition is shown to yield flux concentrations, while solutions subject to a third-type boundary condition yield volume-averaged concentrations. These solutions may be applied with reasonable impunity to finite as well as semi-infinite media if back mixing at the exit is precluded. Implications of the distinction between resident and flux concentrations to laboratory and field studies of solute transport are discussed. It is suggested that perceived limitations of the convection-dispersion model for media with large variations in pore water velocities may in certain cases be attributable to a failure to distinguish between volume-averaged and flux-averaged concentrations.

INTRODUCTION

The convective-dispersive transport equation is the foundation upon which numerous mathematical analyses of solute transport in porous media have been based. Recently, questions have been raised regarding the applicability of this model to media exhibiting large variations in pore water velocities caused by the presence of continuous large pores or by field-scale variability in hydraulic properties [van Genuchten and Wierenga, 1976]. Under certain limiting conditions (i.e., for low apparent dispersivities), all solutions of the classical convection-dispersion model yield symmetrical concentration distributions in time and space. Experiments on fractured or aggregated media, however, yield asymmetrical spatial and temporal concentration distributions with first moments markedly different from those anticipated for symmetric distributions [e.g., Bouma and Wösten, 1979]. For such media, rapid breakthrough is observed in laboratory column tracer experiments. It is intuitively apparent that a large portion of the pore space is being more or less bypassed, resulting in a discrepancy between the effluent concentration and the volume-averaged resident pore fluid concentration in the vicinity of the exit boundary. Such a discrepancy is often regarded as incongruous with the classical convection-dispersion equation, a view seemingly corroborated by the inability of certain solutions of this equation to fit observed breakthrough curves [e.g., Nkedi-Kizza et al., 1983].

Distinctions between flux-averaged effluent and volume-averaged resident concentrations have been made by workers in petroleum and chemical engineering [Brigham, 1974; Kreft and Zuber, 1978, 1979]. We will show that it is of fundamental importance to make such a distinction in order to stipulate boundary conditions appropriate for specific experimental solute detection modes. When the assumptions implicitly invoked by various boundary conditions are given proper consideration and when mass balance constraints are carefully

adhered to, we will find that certain perceived limitations of the convection-dispersion model appear to be mitigated.

THEORY

The usual continuum approach to solute transport in porous media invokes the use of concentrations which represent average quantities of solute occurring in the pore fluid within a finite representative elementary volume of the porous medium [Bear, 1972]. Associating this mean value with its centroid results in the requisite function which is continuously differentiable in space. Consideration of a mass balance for nonreactive solutes in one dimension yields the continuity condition

$$\partial(C_r\theta)/\partial t = -\partial J/\partial x \quad (1)$$

where C_r is the volume-averaged concentration (or resident concentration in the terminology of Kreft and Zuber [1978]) which we specifically distinguish from the flux-averaged concentration C_f , to be discussed shortly, θ is the volumetric water content, t is time, and J is the solute flux density. The constitutive relationship describing J is

$$J = qC_r - D\theta \partial C_r/\partial x \quad (2)$$

where q is the liquid flux density and D is the dispersion coefficient representing the combined effects of diffusion and hydrodynamic dispersion on transport. Combination of (1) and (2) and restriction of our attention to the case of constant q , θ , and D for macroscopically one-dimensional transport yields the linear convection-dispersion equation

$$\frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (3)$$

where $v = q/\theta$ is the mean pore water velocity.

Boundary Conditions for Volume-Averaged Equations

Considerable attention has been given to the solution of (3) for various initial and boundary conditions. For a semi-infinite system, an appropriate lower boundary condition is

$$\partial C_r/\partial x (\infty, t) = 0 \quad (4)$$

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If, on intuitive grounds, we assume that concentrations are continuous across the inlet boundary, and if the input solution is well mixed, a first-type boundary condition results which, for pulse-type injection, would specify

$$\begin{aligned} C_r(0, t) &= C_0 & 0 < t \leq t_0 \\ C_r(0, t) &= 0 & t > t_0 \end{aligned} \quad (5)$$

Although intuitively appealing, we will show that this first-type boundary condition for C_r , defined by (5) is improperly posed. When the input solution is not well mixed, a boundary layer may develop in the region external to the porous medium, rendering (5) inappropriate. However, a more general argument against the applicability of the first-type boundary condition may be posed by consideration of the physical reality underlying the representation of boundaries in mathematical continua. It is apparent that the plane which we regard as the macroscopic boundary has no physical relevance at the microscopic level as irregularities in pore structure and morphology become manifest. If the representative elementary volume (REV) of the porous medium has a diameter l , then because properties in a continuum are associated with the centroid of the averaging volume, medium properties must vary continuously from those of the external medium to those of the bulk porous medium over a finite transition zone of thickness $l/2$ [Bear and Bachmat, 1982]. Integration of (3) over this finite transition zone from $x = 0$ to $x = l/2$ for $t < t_0$ leads to

$$\begin{aligned} qC_0 - D_0\theta(0) \frac{\partial C_r(0, t)}{\partial x} &= qC_r(l/2, t) - D\theta(l/2) \frac{\partial C_r(l/2, t)}{\partial x} \\ &+ \int_0^{l/2} \frac{\partial C_r(x, t)\theta(x)}{\partial t} dx \end{aligned} \quad (6)$$

where D_0 is the bulk solution molecular diffusion coefficient, D is the bulk porous medium dispersion coefficient, and $\theta(x)$ is the volumetric water content at x with $\theta(0) = 1$ and $\theta(l/2)$ the bulk porous medium value. For a well-mixed input solution, $\partial C_r(0, t)/\partial x = 0$. Evaluation of the integral in (6) requires a knowledge of C_r and hence D in the boundary region $0 < x < l/2$. The case of an assumed linear variation in D within a boundary region was discussed by Pearson [1959] who noted that the indeterminacy of this function makes it desirable to impose the limiting condition that $l \rightarrow 0$, causing the integral to vanish. Taking l as infinitesimal in (6) and proceeding in a similar fashion for $t > t_0$ yields, directly,

$$\begin{aligned} \left(C_r - \frac{D}{v} \frac{\partial C_r}{\partial x} \right) \Big|_{x=0^+} &= C_0 & 0 < t \leq t_0 \\ \left(C_r - \frac{D}{v} \frac{\partial C_r}{\partial x} \right) \Big|_{x=0^+} &= 0 & t > t_0 \end{aligned} \quad (7)$$

which is the third-type boundary condition for pulse injection specifying the solute flux at the inlet boundary. We will refer to the quantity D/v as the apparent medium dispersivity. The designation 0^+ denotes quantities evaluated approaching $x = 0$ from positive x (interior to the porous medium).

We may interpret the third-type boundary condition to imply the existence of a transition region within which medium dispersivity and concentration vary continuously. The transition region is treated macroscopically as being of infinitesimal thickness, resulting in apparent discontinuities in both quantities at the boundary. Actual concentrations at the

pore scale will vary continuously over the finite transition region. The incongruity of a concentration discontinuity at the boundary which increases with the apparent dispersivity must be tempered by the realization that calculated values have no physical relevance within $l/2$ of the boundary. To derive the first-type boundary condition for C_r , (equation (5)) from (6), an additional assumption to those involved for the third-type condition must be made, namely, that $\partial C_r/\partial x = 0$ interior to the transition zone. Because this latter stipulation will not be met, we find that the cost of maintaining macroscopic continuity of concentration for the first-type condition is a loss of mass flux continuity. Considering the indeterminant nature of the microscopic features of the boundary transition region, the least we can do is require that the basic condition of mass conservation be met by the boundary conditions.

The solution to (3), subject to the initial conditions,

$$C_r(x, 0) = 0 \quad (8)$$

and the third-type upper boundary condition (7) for the semi-infinite case (4) has been given by Lindstrom *et al.* [1967] as

$$\begin{aligned} C_r(x, t) &= C_0 A(x, t) & 0 < t \leq t_0 \\ C_r(x, t) &= C_0 A(x, t) - C_0 A(x, t - t_0) & t > t_0 \end{aligned} \quad (9a)$$

where

$$\begin{aligned} A(x, t) &= \frac{1}{2} \operatorname{erfc} \left[\frac{x - vt}{2(Dt)^{1/2}} \right] + \left[\frac{v^2 t}{\pi D} \right]^{1/2} \exp \left[\frac{-(x - vt)^2}{4Dt} \right] \\ &- \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{D} \right) \exp(vx/D) \operatorname{erfc} \left[\frac{x + vt}{2(Dt)^{1/2}} \right] \end{aligned} \quad (9b)$$

which is the appropriate expression for evaluating volume-averaged resident concentrations.

It may be noted that a commonly employed solution for C_r is obtained by truncating the last two terms from $A(x, t)$, thus leaving only the first erfc term. This solution may be derived explicitly if the porous medium is assumed to extend to infinity in both directions from the injection plane. The resulting spatial distribution of C_r as $t_0 \rightarrow 0$ yields a normal curve with a first moment occurring at $x = vt$. The symmetry of this distribution is disturbed by inlet boundaries that preclude back dispersion and skew the solute distribution away from the boundary.

Transformation to Flux-Averaged Equations

In many cases, solute flux distributions rather than pore fluid concentrations may be of primary interest. It is then convenient to define the flux-averaged concentration C_f such that

$$qC_f = J \quad (10)$$

or, with (2),

$$C_f = C_r - \frac{D}{v} \frac{\partial C_r}{\partial x} \quad (11)$$

which is valid for nonzero pore water velocities. Flux concentrations may be interpreted physically as representing the mean of the microscopic fluid concentrations weighted by their respective microscopic fluid velocities. The discrepancy between C_f and C_r increases with the apparent dispersivity [Kreft and Zuber, 1978]. In the special case of $v = 0$ with

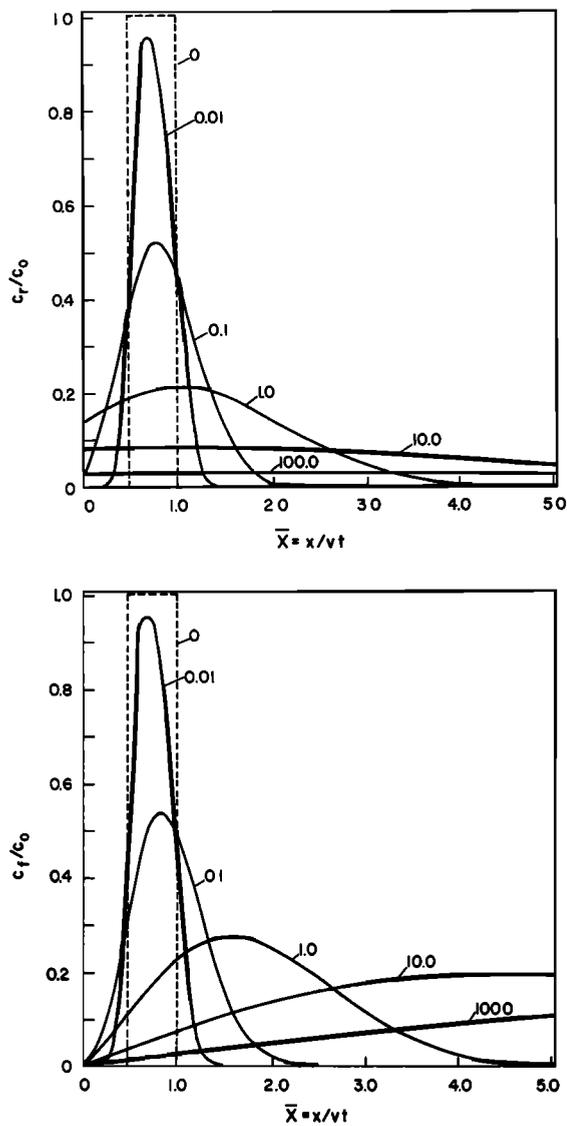


Fig. 1. (a) Resident concentrations by (9) and (b) flux concentrations by (18) as functions of dimensionless distance for a pulse of duration $vt_0 = 0.5$ m at a final time $vt = 1.0$ m for various apparent dispersivities D/v (values indicated on curves).

mixing solely by diffusion, C_f has no physical relevance and is mathematically undefined.

To evaluate $C_f(x, t)$ for a semi-infinite medium, we may employ a transformation of (3), (4), (5), and (8). Putting (10) into (1) for constant (and nonzero) v yields

$$\frac{\partial C_r}{\partial t} = -v \frac{\partial C_f}{\partial x} \quad (12)$$

Differentiating (11) with respect to time yields

$$\frac{\partial C_f}{\partial t} = \frac{\partial C_r}{\partial t} - \frac{D}{v} \frac{\partial^2 C_r}{\partial x^2} \quad (13)$$

Use of (12) to eliminate C_r from (13) gives

$$\frac{\partial C_f}{\partial t} = D \frac{\partial^2 C_f}{\partial x^2} - v \frac{\partial C_f}{\partial x} \quad (14)$$

which is mathematically identical to (3) but with C_r replaced by C_f . Both equations describe the same physical processes, and D and v represent precisely the same physical quantities in

both equations. This duality of interpretation of the physical meaning of the concentrations in the convection-dispersion equation imposes a need to carefully stipulate boundary conditions in keeping with the desired meaning. The identical mathematical form of (3) and (14) must not be allowed to obscure the fundamental distinction between resident and flux concentrations.

For the initial condition $C_r = 0$ we have by differentiation that $\partial C_r / \partial x = 0$, which leads to the transformed initial condition in terms of C_f by direct substitution in (11):

$$C_f(x, 0) = 0 \quad (15)$$

The lower boundary condition $\partial C_r / \partial x = 0$ transforms subject to the stipulation that higher order spatial derivatives of C_r are also zero at $x = \infty$, to yield

$$\frac{\partial C_f}{\partial x}(\infty, t) = 0 \quad (16)$$

To evaluate the transformed upper boundary condition, we eliminate C_r from (7) with (11), which gives, immediately,

$$\begin{aligned} C_f(0, t) &= C_0 & 0 < t \leq t_0 \\ C_f(0, t) &= 0 & t > t_0 \end{aligned} \quad (17)$$

The transformation from C_r to C_f results in a mathematically identical set of equations with the exception of the upper boundary condition which changes from a third-type condition for C_r to a first-type for C_f . The solution of (14)–(17) is

$$\begin{aligned} C_f(x, t) &= C_0 B(x, t) & 0 < t \leq t_0 \\ C_f(x, t) &= C_0 B(x, t) - C_0 B(x, t - t_0) & t > t_0 \end{aligned} \quad (18a)$$

where

$$B(x, t) = \frac{1}{2} \operatorname{erfc} \left[\frac{x - vt}{2(Dt)^{1/2}} \right] + \frac{1}{2} \exp(vx/D) \operatorname{erfc} \left[\frac{x + vt}{2(Dt)^{1/2}} \right] \quad (18b)$$

Obviously, the problem posed by (14)–(17) may be solved mathematically, irrespective of the subscript on C . In fact, (18) is most commonly presented as a solution to the volume-averaged equations for the semi-infinite case subject to a first-type upper boundary condition in C_r (equation (5)) [Lapidus and Amundson, 1952]. The form of (18) is then preserved, but the result is interpreted as representing $C_f(x, t)$ rather than $C_r(x, t)$. By conceding on physical grounds that a flux-type input boundary condition must be employed (i.e., the third type in C_r), we see that the foregoing interpretation of (18) is incorrect. Application of this equation implies that a transformation has been made from volume-averaged to flux-averaged concentrations.

RESULTS AND DISCUSSION

Spatial Concentration Distributions

Figure 1 compares the spatial distributions of C_r and C_f in the x direction calculated from (9) and (18), respectively, using apparent dispersivities (D/v) that range from 0.01 to 100.0 m. Reduced concentrations C_r/C_0 and C_f/C_0 are plotted against the dimensionless distance $\bar{X} = x/vt$ for a pulse of duration $vt_0 = 0.5$ m and a final time given by $vt = 1.0$ m.

It is apparent that all curves for C_f pass through the origin in accordance with the boundary condition $C_f(x, t) = 0$ for $t > t_0$. This is not the case for the C_r curves, which exhibit an apparent discontinuity in concentration at the inlet boundary

TABLE 1. First Moments of Spatial Distributions $\langle \bar{X} \rangle$ and Modal Distances \bar{X}_m as Ratios With the Piston Front Center of Gravity X^* for Various Apparent Dispersivities D/v With $vt_0 = 0.5$ m and $vt = 1.0$ m

D/v , m	$\langle \bar{X} \rangle / X^*$		\bar{X}_m / X^*	
	C_r	C_f	C_r	C_f
0.01	1.01	1.03	0.98	0.97
0.1	1.13	1.26	1.04	1.17
1.0	1.88	2.51	1.29	2.13
10.0	4.62	6.83	1.58	5.47
100.0	13.44	20.61	1.78	16.19

which increases in magnitude with the dispersivity as expected.

For the lowest dispersivity medium the C_r and C_f curves are very similar (Figure 1). Mathematically, it is apparent from the definition of C_f that as $D/v \rightarrow 0$, $C_f \rightarrow C_r$. Physically, this reflects the fact that volume-averaged and flux-averaged concentrations become identical when variations in microscopic pore water velocities tend to zero. As these velocity variations increase, dispersive transport dominates over macroscopically convective transport, and the spatial distributions of C_r and C_f gradually diverge. Both distributions become markedly asymmetrical, exhibiting skewing away from the injection boundary. This skewing forces the modal and mean values of C_r and C_f to occur at greater distances from the injection boundary than would be the case for purely convective transport.

For piston flow ($D = 0$) the distributions of C_r and C_f reduce to a square wave with a reduced concentration of unity between $\bar{X} = 0.5$ and $\bar{X} = 1.0$ (Figure 1). The first moment in space for piston flow accordingly occurs at $\bar{X} = 0.75$. We will designate this value of \bar{X} , corresponding to the center of mass for piston flow, as X^* . The first moments of the spatial distributions of C_r and C_f may be calculated as:

$$\langle \bar{X} \rangle = \left[\int_0^\infty \bar{X} C(\bar{X}) d\bar{X} \right] \left[\int_0^\infty C(\bar{X}) d\bar{X} \right]^{-1} \quad (19)$$

where C is C_r or C_f and $\langle \bar{X} \rangle$ is the dimensionless distance corresponding to the mean of the distribution function. For resident concentrations, $\langle \bar{X} \rangle$ describes the center of mass of the solute distribution, while for C_f the value represents the distance at which the solute flux density attains its mean value.

Values of $\langle \bar{X} \rangle$ were evaluated from (19) by numerical quadrature for the cases presented in Figure 1. Results are given in Table 1 as $\langle \bar{X} \rangle / X^*$ values representing ratios of actual first moments of the spatial distributions to those for piston flow. Also given are reduced modal distances \bar{X}_m / X^* corresponding to maxima in the C_r and C_f distributions. The first moments of C_r increase markedly beyond the piston flow mean as apparent dispersivity increases, while modal distances advance more gradually, lagging well behind mean distances. Mean and modal distances for distributions of C_f likewise increase with increasing dispersivity. Note that the modal values for C_f increase much more with increasing dispersivity than the values for C_r . Also, modal and mean values for C_f occur at larger distances than those for C_r at a given dispersivity.

It is often not appreciated that the convection-dispersion equation predicts centers of mass of concentration profiles in excess of those expected for piston flow. Analyses of solute transport are sometimes made by explicitly or implicitly de-

coupling convection and dispersion mechanisms [Sidle and Kardos, 1979; Rose et al., 1982]. The center of mass is assumed to move at a velocity v with symmetric dispersion occurring about the mean. This decoupling is mathematically equivalent to imposing boundary conditions relevant to infinite media. For bounded media, this leads to errors which increase with apparent dispersivity as the last two terms in (9b) for C_r become increasingly significant. In media which exhibit large variabilities in pore water velocities, hydrodynamic dispersion becomes increasingly more important relative to convective transport, and the implied solution truncation will lead to significant errors.

To correct for observed discrepancies between measured centers of mass and piston flow values, bicontinuum models with "mobile" and "immobile" pore regions have been postulated [Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976; Sidle and Kardos, 1979; Rao et al., 1980]. By viewing the data in Table 1 in this manner, we could conclude that for the $D/v = 100$ m medium the "mobile" pore fraction is approximated by $X^* / \langle \bar{X} \rangle$ for C_r , i.e., $1/13.44 = 0.074$. This value may or may not have any physical significance, but if the medium is viewed as a simple (mono-) continuum, the information is immaterial. Microscopic features have no direct relevance to the macroscopic description except insofar as they affect the adequacy of the imposed macroscopic boundary conditions. If the scale of microscopic variations in the pore structure governs the REV, which in turn governs the thickness of the boundary transition region, as has been suggested, then the region of validity of a bulk continuum approach will be affected. So long as the flow region of interest is large compared to the scale of the microscopic heterogeneities and hence to the size of the boundary transition region, a monocontinuum approach should be valid. In such circumstances, the exclusion of a portion of the fluid-filled pore space from the porous medium continuum is physically justifiable only if (1) part of the pore fluid is encapsulated by some form of impermeable or semipermeable membrane or (2) electrochemical forces exclude solute near solid surfaces (i.e., negative adsorption).

Temporal Concentration Distributions

In many field and laboratory situations it is either more desirable or convenient to monitor temporal concentration changes at fixed points in space downstream from a tracer injection location rather than to determine spatial distributions at fixed times. Confusion between volume- and flux-averaged concentrations in such situations may lead to gross misinterpretations of observations. Values of the reduced concentrations of C_r/C_0 and C_f/C_0 are given in Figure 2 as functions of the dimensionless time $T = vt/x$ at a fixed distance $x = 0.1$ m for media subject to a dimensionless pulse duration $vt_0/x = 0.5$ and characterized by various values of the dimensionless group D/vx . (For the sake of parallelism with the spatial distribution curves given for various D/v , we employ the dimensionless group D/vx in lieu of its inverse, which represents a Peclet number.) As was observed for the spatial distribution functions, the temporal distributions of C_r and C_f become indistinguishable as the apparent dispersivity approaches zero (piston flow). As dispersivity increases, peak values of both C_r and C_f shift to shorter times. However, while the temporal distribution of resident concentrations becomes increasingly flat, values of C_f pass through a minimum at intermediate D/v . In the limit as $D/v \rightarrow \infty$, C_r becomes zero at all times while the distribution of C_f converges to a square wave with unit concentration between $T = 0$ to 0.5 (Figure 2). To use the

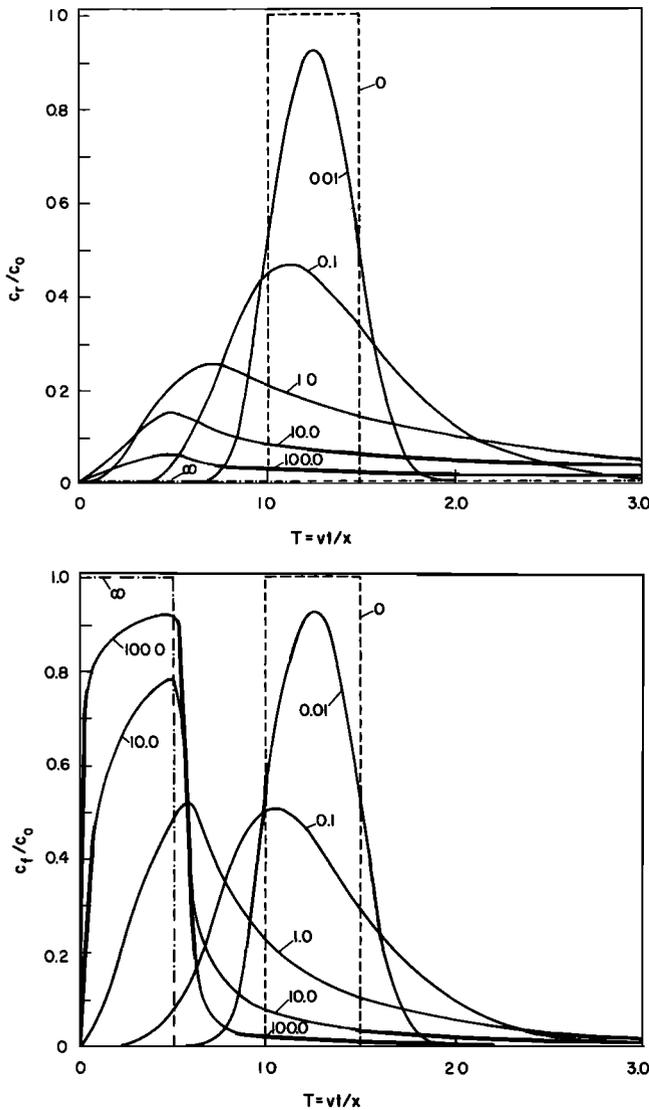


Fig. 2. (a) Resident concentrations by (9) and (b) flux concentrations by (18) as functions of dimensionless time at $x = 0.1$ m for a pulse duration $vt_0/x = 0.5$ and for various values of D/vx (values indicated on curves).

terminology of *Bouma and Dekker* [1978] a "short-circuit" of zero impedance occurs, and the flux conditions imposed at $x = 0$ are instantaneously propagated throughout the medium. As with the piston flow scenario, this limiting case may be approached but, of course, never achieved.

The marked differences between temporal distributions of C_r and C_f have important but generally unappreciated implications to the interpretation of laboratory tracer experiments as well as for field lysimeter and observation well data. Consider the case of transport through a finite soil column during steady water flow. Effluent solution is collected as it exits the column, and its concentration is determined as a function of time. To properly interpret the measured concentrations, it must be recognized that the values represent flux-averaged and not pore volume-averaged quantities. This is intuitively apparent if one considers the extreme case of flow through a fractured porous medium exhibiting large variations in microscopic pore water velocities. The effluent solution comes nearly exclusively from the larger pores, which "short-circuit" the input solution resulting in rapid breakthrough and ex-

tended "tailing." However, the volume-averaged concentration within the column near the outflow boundary may be much less than that of the flux-averaged effluent solution, particularly during the peak effluent concentration phase.

To pose macroscopic boundary conditions for the exit boundary, we may proceed in the same manner as for the inflow boundary by imposing a flux continuity and assuming an infinitesimal boundary transition region, to obtain

$$C_e = \left(C_r - \frac{D}{v} \frac{\partial C_r}{\partial x} \right) \Big|_{x=L^-} \quad (20)$$

where $C_e = C_e(t)$ is the concentration in the effluent and L^- denotes that the quantities are evaluated approaching L from the interior of the porous medium. It is evident that C_e is precisely the definition of C_f at $x = L$ given by (11). Thus the analytical solution for C_f given by (18) is to be used for C_e provided that we assume that C_r for $x < L$ is unaffected by the additional condition imposed on the solution that the spatial derivatives of C_r are zero at $x = \infty$. This provision imposes a mild restriction, since the outflow boundary of a column should have no effect on the upstream velocity distribution interior to the boundary layer during steady flow. If no back mixing occurs, then the solute distribution interior to the column will be unaffected by the boundary. Since the only mechanism of back mixing is diffusion, little error should result when hydrodynamic dispersion is the dominant mechanism of dispersion in the porous medium. In most practical instances, this will be the case.

Equating C_e and C_f and employing (18) to describe the effluent-time data indicates that Figure 2b may be interpreted as a family of breakthrough curves for columns of specified length $x = L$. The dimensionless time T corresponds physically to the number of pore volumes of effluent. It should be mentioned that (18) often has been employed to describe effluent concentrations from column tracer experiments but on the grounds that it represents $C_r(x, t)$ and that $C_r(L, t) = C_f(L, t)$. This reasoning is incorrect, although the result is fortuitously identical so long as only flux concentrations are dealt with. However, the implication that C_r and C_f are identical will lead to gross errors if subsequent predictions of C_r are made. Since the assumption that $C_r(L, t) = C_f(L, t)$ is intuitively unreasonable for fractured porous media, it has been assumed frequently that a monocontinuum approach in such media is infeasible. The curves of Figure 2b show that the rapid breakthrough and tailing typical of such systems are, in fact, predicted by the flux concentration solution (18) for media of high dispersivity.

If the observation scale is large compared to the scale of heterogeneity, it should be feasible to model the porous medium as a monocontinuum and employ (18) to determine transport coefficients from effluent breakthrough curves [e.g., *van Genuchten*, 1981; *Parker and van Genuchten*, 1984]. For subsequent predictions of $C_r(x, t)$, these coefficients may be employed with (9). Use of (18) to predict $C_r(x, t)$ on the assumption that $C_r = C_f$ will lead to gross errors for high-dispersivity media. If experimental values of C_r are desired, appropriate extraction of sectioned columns must be performed.

It is noteworthy that the area under the curves of C_f versus T from $T = 0$ to ∞ is constant and equal to the dimensionless pulse time $vt_0/x = 0.5$ (Figure 2b). This indicates that the solution meets the mass balance criteria:

$$\int_0^x C_r(\chi, t) d\chi = v \int_0^t [C_0 - C_f(x, \tau)] d\tau \quad (21a)$$

$$0 < t \leq t_0$$

$$\int_0^x C_r(\chi, t) d\chi = v \int_0^{t_0} C_0 d\tau - v \int_0^t C_f(x, \tau) d\tau \quad (21b)$$

$$t > t_0$$

for any particular values of x and t where χ and τ are dummy variables. For $x = L$, this simply states that the solute mass in the column equals the difference between cumulative inflow and outflow. In the limit as $t \rightarrow \infty$, the left-hand side of (21) goes to zero, and from the definition of $T = vt/x$, we obtain

$$\frac{vt_0}{x} = \int_0^\infty \frac{C_f}{C_0} dT \quad (22)$$

which is the observed result.

Note that the integral in (22) involves C_f , not C_r . In some cases, solutions for C_r have been employed to analyze effluent concentration data [e.g., *Nkedi-Kizza et al.*, 1983]. With C_r substituted for C_f in (22), an inequality is obtained with the left-hand side always less than the right-hand side. This has the effect of making the apparent pore water velocity seem greater than the actual value to force a mass balance (i.e., retardation factors less than unity). The erroneous inference to be drawn is that some of the pore volume apparently excludes solute. This difficulty is not obtained when the solution appropriate to the flux detection mode is employed.

It is useful to also note that by differentiating (21) with respect to time or space, two additional transformations between resident and flux concentrations are obtained; these transformations may be regarded as supplemental but fundamentally equivalent to that of (11), namely,

$$\int_0^x \frac{\partial C_r(\chi, t)}{\partial t} d\chi + vC_f(x, t) = vC_0 \quad 0 < t \leq t_0 \quad (23a)$$

$$\int_0^x \frac{\partial C_r(\chi, t)}{\partial t} d\chi + vC_f(x, t) = 0 \quad t > t_0 \quad (23b)$$

$$C_r(x, t) = -v \int_0^t \frac{\partial C_f(x, \tau)}{\partial x} d\tau \quad t > 0 \quad (24)$$

The solutions which we have presented for C_r and C_f satisfy these mass balance constraints. Solutions which fail to distinguish between C_r and C_f generally will not satisfy these criteria. This is notably the case for solutions commonly applied to column tracer studies which assume that the effluent concentration is equal to the resident concentration at $x = L$. An exception arises for the solution of the convection-dispersion equation given by *Brenner* [1962]. This solution imposes a third-type upper boundary condition and a zero gradient condition at $x = L$ for C_r . Equation (7) and (20) are thus satisfied; however, the assumption that $\partial C_r(L, t)/\partial x = 0$ forces the concentration to be continuous at the outflow as (20) reduces to $C_e(t) = C_r(L, t)$. Use of *Brenner's* solution for C_r and evaluation of C_f using (11) satisfies the conditions stipulated by (23) and (24) [*van Genuchten and Parker*, 1984]. Predicted concentrations at $x = L$ thus yield physically acceptable estimates of C_e from a mass balance standpoint. However, the assumption of concentration continuity at the exit seems inconsistent with the macroscopic treatment of the upper boundary at which the concentration is discontinuous. The rationalization of the zero gradient condition at the out-

flow presumably arises from the intuitive argument that boundary layers cannot occur at outflow boundaries. Boundary layers external to porous media resulting from poor mixing of outflow solution indeed cannot occur. However, boundary layers may arise from the more general conception of boundary layers as transition regions within which transport parameters change from those of the bulk porous medium to those of the bulk solution. Accordingly, a macroscopic concentration discontinuity at exit boundaries may be anticipated in high-dispersivity media, and the solutions formally derived from semi-infinite systems may be expected to provide a more suitable approximation of the boundary than *Brenner's* explicitly finite solution, which imposes a zero gradient condition at the column exit.

This rather heuristic argument against the applicability of *Brenner's* finite column solution is reinforced by consideration of the limiting case as $D/v \rightarrow \infty$, which yields for *Brenner's* solution at $x = L$,

$$\begin{aligned} C_e/C_0 &= 1 - e^{-T} & T \leq T_0 \\ C_e/C_0 &= e^{T_0-T} - e^{-T} & T > T_0 \end{aligned} \quad (25)$$

while (18) yields, in the limit,

$$\begin{aligned} C_e/C_0 &= 1 & T \leq T_0 \\ C_e/C_0 &= 0 & T > T_0 \end{aligned} \quad (26)$$

where $C_e = C_e(t) = C_f(L, t)$ is the effluent concentration, $T = vt/L$ is the eluted pore volumes, and $T_0 = vt_0/L$ is the reduced pulse duration. Equation (25) describes a breakthrough curve (C_e/C_0 versus T) which for a continuous wave passes through the origin, gradually increases to $C_e/C_0 = 0.632$ at $T = 1.0$, and approaches $C_e/C_0 = 1.0$ as $T \rightarrow \infty$. This function contrasts sharply with the square wave for the limiting case described by (26) (Figure 2b). *Brenner's* solution is incapable of predicting this "short-circuiting" behavior which, as previously mentioned, fractured porous media are observed to approach. This diminishes the utility of *Brenner's* solution and throws further doubt on the appropriateness of the assumptions it invokes in posing the lower boundary condition.

Analogous problems to those occurring in laboratory studies arise in the interpretation of solution concentrations in samples taken from wells or lysimeters in the field. The least ambiguous field measurements are those obtained from large monolithic pan lysimeters which yield flux concentrations for a well-defined flow region. The effect of the exit boundary on the flow pattern, particularly for unsaturated conditions, is the only uncertainty (so long as the results are not extended beyond the bounds of the monolith). Subphreatic well samples are also most appropriately viewed as (local) flux concentrations. Their significance to the interpretation of aquifer properties will depend on the formation's homogeneity and the magnitude of flow disturbances caused by the well. The interpretation of results from samples taken with small suction lysimeters in the unsaturated zone is much less certain. Depending on the manner in which these units disrupt the local flow pattern, the sampled concentrations may yield resident concentrations or flux concentrations or anything in between.

An additional complication to the interpretation of field solution samples arises because the sampled quantities generally represent a small proportion of the total flow region of interest. If the scale of variability of pore water velocity is greater than the effective radius of the sampling device, then multiple samples will need to be taken to evaluate field-scale

areal averages of C_r or C_f . Since scales of hydraulic property variations in geologic media are generally orders of magnitude larger than typical sampling devices, the need for numerous sampling locations is assured.

Caution should be exercised in the interpretation of areally averaged solute concentrations. While resident concentrations may be meaningfully averaged to obtain larger (e.g., field-) scale values, simple averages of flux concentrations have no corresponding direct physical interpretation. To define meaningful areally averaged flux concentrations, local concentrations should be weighted by local hydraulic flux values so that (10) remains valid at the larger scale. Of course, the determination of field-scale values of C_r or C_f in no way guarantees their conformance to a deterministic, monocontinuum convection-dispersion model. At some scale of averaging within the plane perpendicular to flow, constraints on such an approach will arise. However, it appears likely that scale limitations may be less severe than has been thought, owing to misapplications and misinterpretations of various boundary conditions in finite and semi-infinite media.

While we have confined our discussion to one-dimensional transport accompanying steady flow, the approach may be generalized. The definition of C_f given by (11) may be extended to multiple dimensions, in which case the vector nature of C_f becomes significant. In general, the flux transformation of the convection-dispersion equation will be valid only for constant D . For transient flow problems, solutions for C_f may be obtained by local application of (11) after solving the nonlinear problem for C_r subject to a flux-type inlet boundary condition.

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