WATER RESOURCES RESEARCH, VOL. 20, NO. 3, PAGES 335–346, MARCH 1984

Some Exact Solutions for Solute Transport Through Soils Containing Large Cylindrical Macropores

M. T. VAN GENUCHTEN

U.S. Salinity Laboratory

D. H. TANG

Exxon Production Research Company

R. GUENNELON

Institut National de la Recherche Agronomique, France

This paper presents several exact and approximate analytical solutions of the equations describing convective-dispersive solute transport through large cylindrical macropores with simultaneous radial diffusion from the larger pores into the surrounding soil matrix. Adsorption effects were included through the introduction of linear isotherms for both the macropore region and the soil bulk matrix. In one formulation the macropores are surrounded by cylindrical soil mantles of finite thickness. Another formulation considers diffusion from a single cylindrical macropore into a radially infinite soil system. A relatively simple but very accurate approximate solution that ignores dispersion in the macropore region is also derived. The various analytical solutions in this paper can be used to calculate temporal and spatial concentration distributions in the macropore system. In addition, approximate solutions are presented for the radial concentration distribution within the adjacent soil matrix. By means of an example, it is demonstrated that at early times, little accuracy is lost when the radially finite soil mantle is replaced by an infinite system.

INTRODUCTION

Large macropores can significantly influence the rate of water and solute movement in field soils, especially during (but not necessarily limited to) conditions near saturation. Experimental evidence of these effects has been documented in various review articles [*Thomas and Phillips*, 1979; *Bouma*, 1981; *Beven and German*, 1982; *Wierenga*, 1982]. Recently, a number of theoretical models for macropore transport have been introduced. Conceptually, these models can be separated conveniently into two broad groups.

In one group of models, solute transport is described more or less from a microscopic point of view. In these models the bulk of the chemical is assumed to be transported through a single and well-defined pore or crack of known geometry, or through the interaggregate voids between well-defined aggregates. In addition, diffusion-type equations are used to describe the transfer of solute from the larger pores into the bulk soil matrix. Examples of this approach using analytical solutions are given by *Rasmuson and Neretnieks* [1980, 1981] for spherical aggregates and by *Skopp and Warrick* [1974], *Tang et al.* [1981], and *Sudicky and Frind* [1982] for rectangular voids. Similar numerical models, applicable to transport through rectangular voids with simultaneous matrix diffusion, were formulated by *Scotter* [1978] and by *Grisak and Pickens* [1980*a*]. *Scotter* [1978] also formulated an approximate numerical model for transport through cylindrical macropores. *Drummond and McNabb* [1972] describe a conceptually similar model applicable to heat flow in fractured media containing either rectangular or cylindrical fissures.

Paper number 3W1858.
0043-1397/84/003W-1858$05.00

In another group of models the exact geometry of the aggregates, or of the voids between them is not considered explicitly; instead, the various-sized cracks and interaggregate pores are lumped together and treated more or less from an empirical and macroscopic point of view. For that purpose, the liquid phase is divided into two regions: one region applies to the larger pores and is characterized by a relatively high average pore water velocity, while the other region applies to the bulk matrix and has a relatively low or zero flow velocity. Solute exchange between the two liquid regions, if present, is described with a quasi-empirical first-order rate expression. Analytical models of this type, here conveniently called "mobile-immobile" type transport models, are described by *Coats and Smith* [1964], *Villermaux and van Swaaij* [1969], *van Genuchten and Wierenga* [1976], *Gaudet et al.* [1977], and *Skopp et al.* [1981], among others.

Mathematically, the mobile-immobile models of the second group are far less complicated than the more exact models of the first group. Unfortunately, it has been recognized that most parameters in these mobile-immobile type models are extremely difficult to estimate by means of independent measurements [*Rao et al.*, 1979]. Generally, elaborate curve-fitting methods [*van Genuchten*, 1981] are needed to estimate the parameters from observed concentration distributions, a problem that raises questions, not only with respect to parameter uniqueness and model verification [*Davidson et al.*, 1980], but also with respect to the usefulness of these models in ultimately predicting solute transport in structured field soils. Hence methods to estimate the coefficients from measurable soil parameters are sorely needed. A first attempt to do this for soils made up of spherical aggregates was carried out by *Rao et al.* [1980*a*].

The transport models described in this paper form part of the first group. Several exact and approximate analytical solutions are presented that describe solute transport

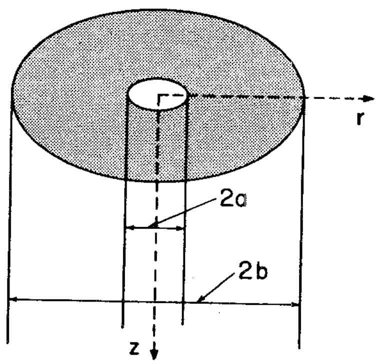

Fig. 1. Schematic picture of a porous medium with a cylindrical macropore.

through well-defined cylindrical macropores with simultaneous diffusion from the larger pores into the surrounding soil matrix. The formulations used here are very similar to those described by *Scotter* [1978], except that the transport equations will be generalized somewhat and solved analytically. Most of the solutions apply to concentration distributions in the macropore system. In addition, two approximate solutions are presented that give the radial concentration distribution within the bulk soil matrix itself.

GOVERNING EQUATIONS

Consider a soil that contains a large number of equally spaced, continuous and cylindrical macropores. The pore has a radius a and is surrounded by a cylindrical soil mantle of radius b (Figure 1). The effective value of b is [*Scotter*, 1978]

$$b = (\pi n_p)^{-1/2} \tag{1}$$

where n_p is the number of pores per unit cross-sectional area perpendicular to the transport direction. The macropores have a local volumetric water content θ_f, while the bulk matrix has a water content of θ_a. When the soil is completely saturated and for well-defined macropores with smooth surfaces, $\theta_f = 1$. However, because of irregular surfaces, local obstructions in the macropore system, or partial desaturation, θ_f generally will be somewhat less than 1, even when the soil is seemingly at saturation. If we denote the volume fraction of macropores in a unit volume of soil by V_f ($= a^2/b^2$) and that of the bulk soil matrix by $V_a = (1 - V_f)$, then the total water content θ is

$$\theta = V_f\theta_f + V_a\theta_a \tag{2}$$

We can also define a mobile (macropore) water content θ_m and an immobile (soil matrix) water content θ_{im}, such that

$$\theta = \theta_m + \theta_{im} \tag{3}$$

where $\theta_m = V_f\theta_f$ and $\theta_{im} = V_a\theta_a$. When the soil is saturated, θ_m and θ_{im} represent the macropore and micropore porosities, respectively. Dividing (3) by θ, we get

$$1 = \theta_m/\theta + \theta_{im}/\theta \equiv \phi_m + \phi_{im} \tag{4}$$

Hence ϕ_m and ϕ_{im} are those fractions of the total water content that are associated with the macropore and micropore regions, respectively.

We will make the assumption that transverse diffusion/dispersion processes in the macropore liquid phase are so pronounced that no cross-sectional concentration gradients are present in this phase. In addition, we assume that convective transport within the micropores of the bulk matrix can be ignored. Without adsorption the general equation for solute transport in the macropore system is then [*Vachaud et al.*, 1976; *Gaudet et al.*, 1977; *van Genuchten and Cleary*, 1979; *Rao et al.*, 1980*b*]

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z} \qquad 0 \le r \le a \tag{5}$$

where C_m and C_{im} represent the average concentrations in the mobile and immobile liquid phases, respectively, D_m is the dispersion coefficient, v_m is the average pore water velocity of the macropore region, t is time, and z is distance. The macropore water velocity is given by

$$v_m = q/\theta_m \tag{6}$$

where q is the volumetric flux density. Transport equations similar to (5) but limited to saturated conditions are discussed by *Coats and Smith* [1964], *Bennett and Goodridge* [1970], and *Passioura* [1971], among many others. The second term of (5) represents a sink term that accounts for solute accumulation in the micropore liquid phase. The average concentration C_{im} of that phase is

$$C_{im}(z, t) = \frac{2}{b^2 - a^2} \int_a^b rC_a(z, r, t)\, dr \tag{7}$$

where C_a is the local concentration in the bulk soil matrix. Solute diffusion in this part of the soil is described by the cylindrical diffusion equation:

$$\frac{\partial C_a}{\partial t} = \frac{D_a}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_a}{\partial r}\right) \qquad a < r \le b \tag{8}$$

where D_a is the soil matrix molecular or ionic diffusion coefficient. The transport equations above are augmented with the auxiliary requirements that concentrations must be continuous at the macropore walls,

$$C_m(z, t) = C_a(z, a, t) \tag{9}$$

and that no diffusion takes place across the outer surface ($r = b$) of the cylindrical soil mantle surrounding the macropore,

$$(\partial C_a/\partial r)(z, b, t) = 0 \tag{10}$$

Equations (5)–(10) describe in mathematical terms convective-dispersive transport of nonadsorbed chemicals through the larger macropores, with simultaneous diffusion into a finite cylindrical soil mantle adjacent to these pores. The equations must be modified when the chemical is also adsorbed by the solid phase.

Adsorption can be included in one of several ways. The simplest case arises when adsorption is limited only to the bulk soil matrix, while no adsorption occurs in the macropore region. Because the internal surface area of the soil matrix is much larger than the surface area of the macropore walls, such an assumption may seem reasonable at first. However, macropore walls frequently are coated with highly reactive materials, for example, with aluminum and iron oxides or with fine clay particles. These materials are in immediate contact with the macropore mobile liquid phase, and their presence could lead to a significant reduction in the apparent solute velocity in the macropores, independently of what happens inside the bulk soil matrix.

The problem now becomes how to include adsorption in the macropore region. One possible approach is to include in the term $\partial C_m/\partial t$ of (5) a "face retardation factor" that is proportional to the surface area of the macropore walls [*Freeze and Cherry,* 1979; *Tang et al.,* 1981]. This approach requires the measurement of the surface area of the macropore walls and some type of equivalent adsorption coefficient, both of which are not easily obtained by means of independent experiments, especially for irregular macropore systems.

A different approach would be to divide, on a mass basis, the adsorption sites into two fractions, one fraction (f_m) that is associated and in close contact with the macropore liquid phase and another fraction ($1 - f_m$) associated with the bulk matrix. For this purpose, let us first redefine (5) for an adsorbing system in the same way as was done by *van Genuchten and Wierenga* [1976]:

$$\theta_m \frac{\partial C_m}{\partial t} + \rho_m \frac{\partial S_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_{im} \frac{\partial S_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z} \tag{11}$$

where S_m and S_{im} are the adsorbed concentrations of the macropore and micropore regions, respectively, and where ρ_m and ρ_{im} are the bulk densities (per unit total volume bulk soil) of these two regions such that

$$\rho = \rho_m + \rho_{im} \tag{12}$$

in which ρ represents the total bulk density of the soil. Equation (12) is analogous to (3) for the water content:

$$\rho_m = V_f \rho_f \qquad \rho_{im} = V_a \rho_a \tag{13}$$

where ρ_f and ρ_a are the local bulk densities of the macropore and micropore soil regions, respectively (i.e., per unit volume macropore and unit volume soil matrix, respectively). Again, for a system containing well-defined cylindrical macropores with smooth and inert walls, $\rho_f = 0$.

Similarly to (7), S_{im} is given by

$$S_{im}(z, t) = \frac{2}{b^2 - a^2} \int_a^b r S_a(z, r, t)\, dr \tag{14}$$

Diffusion in the soil matrix is now described by

$$\theta_a \frac{\partial C_a}{\partial t} + \rho_a \frac{\partial S_a}{\partial t} = \theta_a D_a \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_a}{\partial r} \right) \qquad a < r \le b \tag{15}$$

We assume linear and reversible equilibrium adsorption in both soil regions:

$$S_m = k_m C_m \qquad S_a = k_a C_a \qquad S_{im} = k_{im} C_{im} \tag{16}$$

where k_m and k_a are the appropriate distribution coefficients. From (9) and (14) it follows immediately that $k_{im} = k_a$. The total distribution coefficient k is simply a weighted average of k_m and k_{im}:

$$\rho k = \rho_m k_m + \rho_{im} k_{im} \tag{17}$$

Let

$$f_m = \rho_m k_m / \rho k \tag{18}$$

Hence f_m is the mass fraction of the adsorbed concentration that equilibrates with the macropore liquid phase. This fraction not only accounts for those adsorption sites that are in immediate contact with the mobile liquid phase, but also considers the fact that the reactivity of macropore walls may differ from that of the internal surfaces. Experimentally, it is probably difficult to distinguish between these two phenomena. Note that $\rho_m = f_m \rho$ only if $k = k_m = k_{im}$. In general, however, we have

$$\rho_m k_m = f_m \rho k \qquad \rho_{im} k_{im} = (1 - f_m) \rho k \tag{19}$$

Using the relations above, we can eliminate S_m and S_{im} from (11) and (15):

$$(\theta_m + f_m \rho k) \frac{\partial C_m}{\partial t} + [\theta_{im} + (1 - f_m)\rho k] \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z} \tag{20}$$

$$(\theta_a + \rho_a k_a) \frac{\partial C_a}{\partial t} = \theta_a D_a \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_a}{\partial r} \right) \tag{21}$$

Define the following retardation factors:

$$R_m = 1 + f_m \rho k / \theta_m \qquad R_{im} = 1 + (1 - f_m) \rho k / \theta_{im} \tag{22a}$$

$$R_a = 1 + \rho_a k_a / \theta_a \qquad R = 1 + \rho k / \theta \tag{22b}$$

where R is the total retardation factor of the soil system. Note that

$$\theta_m R_m + \theta_{im} R_{im} = \theta R \tag{23}$$

while one may also verify that $R_{im} = R_a$. Substituting (22*a*) and (22*b*) into (20) and (21) gives

$$\theta_m R_m \frac{\partial C_m}{\partial t} + \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z} \tag{24}$$

$$R_{im} \frac{\partial C_a}{\partial t} = \frac{D_a}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_a}{\partial r} \right) \tag{25}$$

Equations (24) and (25) can be applied also to the situation where the mobile retardation factor R_m is defined per unit surface area of the macropores (see, for example, *Tang et al.* [1981]).

For subsequent analysis it is more convenient to express the governing equations in dimensionless form. For that purpose, define the following dimensionless variables:

$$T = qt/\theta L \tag{26a}$$

$$Z = z/L \tag{26b}$$

$$P_m = v_m L / D_m \tag{27}$$

$$\zeta = r/a \tag{28a}$$

$$\zeta_0 = b/a \tag{28b}$$

$$\gamma = \frac{D_a \theta_{im} L}{a^2 q (1 - \beta) R} = \frac{D_a \theta L}{a^2 q R_{im}} \tag{29a}$$

$$\beta = \theta_m R_m / \theta R \tag{29b}$$

$$c_m = \frac{C_m - C_i}{C_0 - C_i} \quad c_a = \frac{C_a - C_i}{C_0 - C_i} \quad c_{im} = \frac{C_{im} - C_i}{C_0 - C_i} \tag{30}$$

where T is the number of pore volumes leached through a soil profile (or soil column) of depth L, P_m is the Peclet number, C_i is the initial concentration, and C_0 is the input concentration. Both C_i and C_0 are assumed to be constant. With (26)–(30) the dimensionless transport equations become

$$\beta R \frac{\partial c_m}{\partial T} + (1 - \beta) R \frac{\partial c_{im}}{\partial T} = \frac{1}{P_m} \frac{\partial^2 c_m}{\partial Z^2} - \frac{\partial c_m}{\partial Z} \qquad 0 \le \zeta \le 1 \tag{31}$$

$$\frac{\partial c_a}{\partial T} = \frac{\gamma}{\zeta} \frac{\partial}{\partial \zeta} \left(\zeta \frac{\partial c_a}{\partial \zeta} \right) \qquad 1 < \zeta \le \zeta_0 \tag{32}$$

$$c_{im} = \frac{2}{\zeta_0^2 - 1} \int_1^{\zeta_0} \zeta c_a \, d\zeta \tag{33}$$

$$c_m(Z, T) = c_a(Z, 1, T) \tag{34}$$

$$(\partial c_m / \partial \zeta)(Z, \zeta_0, T) = 0 \tag{35}$$

The transport model will be solved for a dimensionless initial concentration of zero,

$$c_m(Z, 0) = c_a(Z, \zeta, 0) = 0 \tag{36}$$

a semi-infinite soil profile,

$$(\partial c_m / \partial Z)(\infty, T) = 0 \tag{37}$$

and for two different boundary conditions at the soil surface: either a first-type (or concentration-type) boundary condition of the form

$$c_m(0, T) = 1 \tag{38a}$$

or a third-type (or flux-type) boundary condition of the form

$$\left(c_m - \frac{1}{P_m} \frac{\partial c_m}{\partial Z} \right) \bigg|_{Z=0} = 1 \tag{38b}$$

The solutions are obtained by means of Laplace transforms:

$$\bar{c}(Z, s) = \int_0^\infty \exp(-sT) c(Z, T) \, dT \tag{39}$$

where s is the Laplace transform variable and $\bar{c}$ is the transform of c with respect to T.

Analytical Solutions

First-Type Input Boundary Condition

First, the analytical solution for boundary condition (38*a*) will be derived. Taking the Laplace transform of (32) and using initial condition (36), we obtain

$$\frac{d^2 \bar{c}_a}{d\zeta^2} + \frac{1}{\zeta} \frac{d\bar{c}_a}{d\zeta} - \frac{s}{\gamma} = 0 \tag{40}$$

which has a general solution of the form

$$\bar{c}_a = C_1 I_0(\omega\zeta) + C_2 K_0(\omega\zeta) \tag{41}$$

where

$$\omega = (s/\gamma)^{1/2} \tag{42}$$

C_1 and C_2 in (41) are constants that must be determined from boundary conditions (34) and (35). Taking the Laplace transforms of these boundary conditions and noting that

$$\frac{d\bar{c}_a}{d\zeta} = \omega [C_1 I_1(\omega\zeta) - C_2 K_1(\omega\zeta)] \tag{43}$$

leads to

$$\bar{c}_a = \bar{c}_m \frac{I_0(\omega\zeta) K_1(\omega\zeta_0) + I_1(\omega\zeta_0) K_0(\omega\zeta)}{I_0(\omega) K_1(\omega\zeta_0) + I_1(\omega\zeta_0) K_0(\omega)} \tag{44}$$

Substituting (44) into the Laplace transform of (33) and integrating leads to

$$\bar{c}_{im} = \frac{2\bar{c}_m M(\omega)}{\omega(\zeta_0^2 - 1) N(\omega)} \tag{45}$$

where

$$M(\omega) = I_1(\omega\zeta_0) K_1(\omega) - I_1(\omega) K_1(\omega\zeta_0) \tag{46a}$$

$$N(\omega) = I_0(\omega) K_1(\omega\zeta_0) + I_1(\omega\zeta_0) K_0(\omega) \tag{46b}$$

Taking the Laplace transform of (31) subject to initial condition (36) and substituting (45) in the resulting expression gives

$$\frac{d^2 \bar{c}_m}{dZ^2} - P_m \frac{d\bar{c}_m}{dZ} - P_m \left[s\beta R + \frac{2s(1 - \beta) R M(\omega)}{\omega(\zeta_0^2 - 1) N(\omega)} \right] \bar{c}_m = 0 \tag{47}$$

which must be solved subject to

$$(d\bar{c}_m / dZ)(\infty, s) = 0 \tag{48a}$$

$$\bar{c}_m(0, s) = 1/s \tag{48b}$$

The solution for $\bar{c}_m$ is

$$\bar{c}_m(Z, s) = \frac{1}{s} \exp\left[\tfrac{1}{2} P_m Z - Z\Omega(s)\right] \tag{49}$$

where

$$\Omega(s) = \left[\tfrac{1}{4} P_m^2 + s\beta R P_m + \frac{2P_m (\gamma s)^{1/2} (1 - \beta) R M(\omega)}{(\zeta_0^2 - 1) N(\omega)} \right]^{1/2} \qquad \omega = (s/\gamma)^{1/2} \tag{50}$$

Equation (49) is the Laplace transform solution for the concentration in the macropore liquid phase. The inverse of (49) is

$$c_m(Z, T) = \frac{1}{2\pi i} \int_{\alpha - i\infty}^{\alpha + i\infty} \exp(sT) \bar{c}_m(Z, s) \, ds$$

$$= \frac{\exp(\tfrac{1}{2} P_m Z)}{2\pi i} \int_{\alpha - i\infty}^{\alpha + i\infty} \frac{1}{s} \exp[sT - Z\Omega(s)] \, ds \tag{51}$$

From (46*b*) and (50) it is apparent that a number of singularities are present in (50). Following methods similar to those used by *Rosen* [1952] and *Rasmuson and Neretnieks* [1980], it is readily demonstrated that the term N in $\Omega(s)$ has an infinite number of zeros along the negative real axis. These points are located at

$$s = -\gamma\sigma_n^2 \qquad n = 1, 2, \cdots \tag{52}$$

where σ_n are the roots of

$$J_0(\sigma_n)Y_1(\sigma_n\zeta_0) - Y_0(\sigma_n)J_1(\sigma_n\zeta_0) = 0 \tag{53}$$

Because these roots are all real and positive [*Carslaw and Jaeger,* 1959], the corresponding essential singularities of $\Omega(s)$ are located along the negative real axis. Hence $\bar{c}_m$ is analytic for Re $(s) \geq 0$, except at $s = 0$, and the path of integration can be taken along the imaginary axis ($\alpha = 0$) with a small semicircle Γ of radius $\varepsilon \to 0$ that excludes the origin. For that purpose, (51) is first rewritten in the form

$$c_m = \frac{\exp(\frac{1}{2}P_mZ)}{2\pi i}\lim_{\varepsilon\to 0}\left(\int_{-i\infty}^{-i\varepsilon} + \int_{i\varepsilon}^{i\infty} + \int_{-i\varepsilon}^{i\varepsilon}\right) \cdot \frac{1}{s}\exp[sT - Z\Omega(s)]\, ds \tag{54}$$

Letting $\varepsilon \to 0$, it is readily shown that

$$\frac{\exp(\frac{1}{2}P_mZ)}{2\pi i}\lim_{\varepsilon\to 0}\int_{-i\varepsilon}^{i\varepsilon}\frac{1}{s}\exp[sT - Z\Omega(s)]\, ds = \tfrac{1}{2} \tag{55}$$

The first and second integrals of (54) can be combined by first making the substitutions $s = -i\tau$ and $s = i\tau$, respectively, and then taking the limit

$$c_m = \tfrac{1}{2} + \frac{\exp(\frac{1}{2}P_mZ)}{2\pi}\int_0^\infty \frac{1}{i\tau}\{\exp[i\tau T - Z\Omega(i\tau)] - \exp[-i\tau T - Z\Omega(-i\tau)]\}\, d\tau \tag{56}$$

or

$$c_m = \tfrac{1}{2} + \frac{1}{\pi}\exp(\tfrac{1}{2}P_mZ)\int_0^\infty \text{Re}\left\{\frac{1}{i\tau}\exp[i\tau T - Z\Omega(i\tau)]\right\} d\tau \tag{57}$$

where Re indicates that only the real part of the argument is needed (the imaginary part drops out). Next, the term $\Omega(i\tau)$ in (57) is simplified. To do this, we will make use of the following relationships [*McLachlan,* 1961]:

$$I_0(xi^{1/2}) = \text{Ber}(x) + i\,\text{Bei}(x) \tag{58a}$$

$$I_1(xi^{1/2}) = -i\,\text{Ber}_1(x) + \text{Bei}_1(x) \tag{58b}$$

$$K_0(xi^{1/2}) = \text{Ker}(x) + i\,\text{Kei}(x) \tag{58c}$$

$$K_1(xi^{1/2}) = i\,\text{Ker}_1(x) - \text{Kei}_1(x) \tag{58d}$$

Let us define λ as

$$\lambda = (\tau/\gamma)^{1/2} \tag{59}$$

Using (46*a*), (58*b*), and (58*d*), the term M in (50) can now be written in the form (note that $s = i\tau$)

$$\begin{aligned} M(\lambda i^{1/2}) &= I_1(\lambda\zeta_0 i^{1/2})K_1(\lambda i^{1/2}) - I_1(\lambda i^{1/2})K_1(\lambda\zeta_0 i^{1/2}) \\ &= [-i\,\text{Ber}_1(\zeta_0\lambda) + \text{Bei}_1(\zeta_0\lambda)][i\,\text{Ker}_1(\lambda) - \text{Kei}_1(\lambda)] \\ &\quad - [-i\,\text{Ber}_1(\lambda) + \text{Bei}_1(\lambda)][i\,\text{Ker}_1(\zeta_0\lambda) - \text{Kei}_1(\zeta_0\lambda)] \\ &= M_1 + iM_2 \end{aligned} \tag{60}$$

where

$$\begin{aligned} M_1(\lambda) &= \text{Ber}_1(\zeta_0\lambda)\,\text{Ker}_1(\lambda) - \text{Bei}_1(\zeta_0\lambda)\,\text{Kei}_1(\lambda) \\ &\quad - \text{Ker}_1(\zeta_0\lambda)\,\text{Ber}_1(\lambda) + \text{Kei}_1(\zeta_0\lambda)\,\text{Bei}_1(\lambda) \end{aligned} \tag{61a}$$

$$\begin{aligned} M_2(\lambda) &= \text{Ber}_1(\zeta_0\lambda)\,\text{Kei}_1(\lambda) + \text{Bei}_1(\zeta_0\lambda)\,\text{Ker}_1(\lambda) \\ &\quad - \text{Ker}_1(\zeta_0\lambda)\,\text{Bei}_1(\lambda) - \text{Kei}_1(\zeta_0\lambda)\,\text{Ber}_1(\lambda) \end{aligned} \tag{61b}$$

Similarly,

$$N(\lambda i^{1/2}) = N_1 + iN_2 \tag{62}$$

where

$$\begin{aligned} N_1(\lambda) &= -\text{Kei}_1(\zeta_0\lambda)\,\text{Ber}(\lambda) - \text{Ker}_1(\zeta_0\lambda)\,\text{Bei}(\lambda) \\ &\quad + \text{Bei}_1(\zeta_0\lambda)\,\text{Ker}(\lambda) + \text{Ber}_1(\zeta_0 x)\,\text{Kei}(\lambda) \end{aligned} \tag{63a}$$

$$\begin{aligned} N_2(\lambda) &= \text{Ker}_1(\zeta_0\lambda)\,\text{Ber}(\lambda) - \text{Kei}_1(\zeta_0\lambda)\,\text{Bei}(\lambda) \\ &\quad - \text{Ber}_1(\zeta_0\lambda)\,\text{Ker}(\lambda) + \text{Bei}_1(\zeta_0\lambda)\,\text{Kei}(\lambda) \end{aligned} \tag{63b}$$

Substituting (60) and (62) into $\Omega(i\tau)$, making use of the identity $i^{1/2} = (1 + i)/2^{1/2}$, and simplifying yields

$$\Omega(i\tau) = (\Omega_1 + i\Omega_2)^{1/2} \tag{64}$$

where

$$\Omega_1(\tau) = \tfrac{1}{4}P_m^2 + \frac{P_m(2\gamma\tau)^{1/2}(1-\beta)RA_1}{(\zeta_0^2 - 1)} \tag{65a}$$

$$\Omega_2(\tau) = \beta RP_m\tau + \frac{P_m(2\gamma\tau)^{1/2}(1-\beta)RA_2}{(\zeta_0^2 - 1)} \tag{65b}$$

$$A_1(\lambda) = \frac{N_1(M_1 - M_2) + N_2(M_1 + M_2)}{N_1^2 + N_2^2} \tag{65c}$$

$$A_2(\lambda) = \frac{N_1(M_1 + M_2) - N_2(M_1 - M_2)}{N_1^2 + N_2^2} \tag{65d}$$

The square root function in (64) is evaluated by making use of de Moivre's theorem:

$$\Omega(i\tau) = (r_p)^{1/2}\left[\cos\left(\frac{\theta}{2}\right) + i\sin\left(\frac{\theta}{2}\right)\right] \tag{66}$$

where

$$r_p = (\Omega_1^2 + \Omega_2^2)^{1/2} \tag{67a}$$

$$\theta = \tan^{-1}(\Omega_2/\Omega_1) \tag{67b}$$

Using trigonometric equations, it is readily shown that

$$\cos\left(\frac{\theta}{2}\right) = \left[\tfrac{1}{2}\left(1 + \frac{\Omega_1}{r_p}\right)\right]^{1/2} \tag{68a}$$

$$\sin\left(\frac{\theta}{2}\right) = \left[\tfrac{1}{2}\left(1 - \frac{\Omega_1}{r_p}\right)\right]^{1/2} \tag{68b}$$

and hence

$$\Omega(i\tau) = 2^{-1/2}[(r_p + \Omega_1)^{1/2} + i(r_p - \Omega_1)^{1/2}] \tag{69}$$

Using (69), the argument of the integral in (56) becomes

$$\mathrm{Re}\left[\frac{1}{i\tau}\exp\left(i\tau T - Z\Omega(i\tau)\right)\right]$$

$$= \mathrm{Re}\left\{\frac{-i}{\tau}\exp\left[-\frac{Z}{2^{1/2}}(r_p+\Omega_1)^{1/2}\right]\left\{\cos\left[\tau T - \frac{Z}{2^{1/2}}\cdot(r_p-\Omega_1)^{1/2}\right] + i\sin\left[\tau T - \frac{Z}{2^{1/2}}(r_p-\Omega_1)^{1/2}\right]\right\}\right\}$$

$$= \frac{1}{\tau}\exp\left[-\frac{Z}{2^{1/2}}(r_p+\Omega_1)^{1/2}\right]\sin\left[\tau T - \frac{Z}{2^{1/2}}(r_p-\Omega_1)^{1/2}\right] \quad (70)$$

Finally, substituting (70) into (56) and letting $\tau = \gamma\lambda^2$, we obtain

$$c_m(Z, T) = \tfrac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp\left[\tfrac{1}{2}P_m Z - z_p Z\right] \cdot \sin\left(\gamma\lambda^2 T - z_m Z\right)\frac{d\lambda}{\lambda} \quad (71)$$

where

$$z_p = \left[\tfrac{1}{2}(r_p + \Omega_1)\right]^{1/2} \quad (72a)$$

$$z_m = \left[\tfrac{1}{2}(r_p - \Omega_1)\right]^{1/2} \quad (72b)$$

Note that the analytical solution above has the same structure as the solution derived by *Rasmuson and Neretnieks* [1980] for convective-dispersive transport between spherical particles.

Third-Type Input Boundary Condition

The analytical solution of (31)–(37) for the constant flux-type boundary condition (equation (38*b*)) will now be derived. Using the same procedure as before, the Laplace transform solution for $\bar{c}_m$ was found to be

$$\bar{c}_m(Z, s) = \frac{P_m \exp\left[\tfrac{1}{2}P_m Z - Z\Omega(s)\right]}{s\left[\tfrac{1}{2}P_m + \Omega(s)\right]^{1/2}} \quad (73)$$

where $\Omega(s)$ is given by (50). Comparing (49) and (73), it is apparent that (73) is related to (49) through the expression

$$\bar{c}_{m3}(Z, s) = P_m \exp(P_m Z)\int_Z^\infty \exp(-P_m y)\bar{c}_{m1}(y, s)\, dy \quad (74a)$$

where $\bar{c}_{m1}$ represents the Laplace transform solution for the first-type boundary condition (equation (49)) and $\bar{c}_{m3}$ represents the solution for the third-type boundary condition (equation (73)). Equation (74*a*) also holds for the inverse transforms:

$$c_{m3}(Z, T) = P_m \exp(P_m Z)\int_Z^\infty \exp(-P_m Z)c_{m1}(y, T)\, dy \quad (74b)$$

Substituting (71) for c_{m1} in (74*b*) and integrating hence leads directly to the solution for the third-type boundary condition:

$$c_m(Z, T) = \tfrac{1}{2} + \frac{2P_m}{\pi}\int_0^\infty \frac{\exp\left(\tfrac{1}{2}P_m Z - z_p Z\right)}{\left\{\left[\tfrac{1}{2}P_m + z_p\right]^2 + z_m^2\right\}} \cdot \left[\left(\frac{P_m}{2} + z_p\right)\sin\left(\gamma\lambda^2 T - z_m Z\right) - z_m\cos\left(\gamma\lambda^2 T - z_m Z\right)\right]\frac{d\lambda}{\lambda} \quad (75)$$

Because of conservation of mass, (75) is preferred over (71) when concentration-distance curves in a semi-infinite profile are considered. However, when (75) is applied to breakthrough curves from finite laboratory soil columns or from finite field profiles, it can be shown that the principle of mass conservation will be violated [*Brigham*, 1974; *Baker*, 1977; *Kreft and Zuber*, 1978]. From mass balance considerations and using the same solution for the flux-type boundary condition (equation (75)), it is possible to derive the following general expression for the breakthrough curve, denoted here by c_e:

$$c_e(T) = \left.\left(c_m - \frac{1}{P_m}\frac{\partial c_m}{\partial Z}\right)\right|_{Z=1} \quad (76)$$

The variable c_e is known as the flowing concentration [*Brigham*, 1974] or the flux concentration [*Kreft and Zuber*, 1978], as opposed to the in situ or resident concentration c_m. Substituting (75) into (76) yields exactly the same expression as (71), evaluated at $Z = 1$ ($z = L$):

$$c_e(T) = \tfrac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp\left(\frac{P_m}{2} - z_p\right)\sin\left(\gamma\lambda^2 T - z_m\right)\frac{d\lambda}{\lambda} \quad (77)$$

A Single Macropore in a Radially Infinite System

A slightly different formulation of the transport equations is necessary when the cylindrical soil mantle surrounding a single macropore extends to infinity (b or $\zeta_0 \to \infty$). The transport equation for the macropore is now

$$R_m\frac{\partial c_m}{\partial t} = D_m\frac{\partial^2 c_m}{\partial z^2} - v_m\frac{\partial c_m}{\partial z} - \frac{J_a}{\pi a^2\theta_f} \quad (78)$$

where as before the subscript m refers to the cylindrical macropore, while J_a defines the solute flux from the macropore into the soil matrix:

$$J_a = -2\pi a\theta_a D_a \left.\frac{\partial C_a}{\partial r}\right|_{r=a} \quad (79)$$

In this formulation the macropore retardation factor R_m is best expressed in terms of the surface area of the macropore wall, i.e., analogously to the formulation of *Tang et al.* [1981]. The remaining equations are the same as before, i.e.,

$$R_a\frac{\partial c_a}{\partial t} = \frac{D_a}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_a}{\partial r}\right) \quad (80)$$

for diffusion in the soil matrix, together with the internal boundary conditions

$$c_m(z, t) = c_a(z, a, t) \tag{81a}$$

$$\frac{\partial c_a}{\partial r}(z, \infty, t) = 0 \tag{81b}$$

Analytical solutions of (78)–(81) are given here only in terms of the original variables. The Laplace transform of (80) for an initial condition of zero is

$$\frac{d^2\bar{c}_a}{dr^2} + \frac{1}{r}\frac{d\bar{c}_a}{dr} - \frac{R_a s}{D_a}\bar{c}_a = 0 \tag{82}$$

which, when solved subject to boundary conditions (81*a*) and (81*b*) yields

$$\bar{c}_a = \bar{c}_m K_0(\omega_1 r)/K_0(\omega_1 a) \tag{83}$$

where

$$\omega_1 = (R_a s/D_a)^{1/2} \tag{84}$$

Substituting (84) into the Laplace transform of (79) yields

$$J_a = 2\pi a\theta_a D_a \omega_1 \frac{K_1(\omega_1 a)}{K_0(\omega_1 a)}\bar{c}_m \tag{85}$$

Using (85), the Laplace transform of (78) for an initial condition of zero is

$$\frac{d^2\bar{c}_m}{dz^2} - \frac{v_m}{D_m}\frac{d\bar{c}_m}{dz} - \left[\frac{R_m s}{D_m} + \frac{2\theta_a(D_a R_a s)^{1/2}}{aD_m\theta_f}\frac{K_1(\omega_1 a)}{K_0(\omega_1 a)}\right]\bar{c}_m = 0 \tag{86}$$

For a first-type boundary condition similar to (38*a*), the solution of (86) is

$$\bar{c}_m(z, s) = \frac{1}{s}\exp\left[\frac{v_m z}{2D_m} - z\Phi(s)\right] \tag{87}$$

where

$$\Phi(s) = \left[\frac{v_m^2}{4D_m^2} + \frac{R_m s}{D_m} + \frac{2\theta_a(D_a R_a s)^{1/2}}{aD_m\theta_f}\frac{K_1(\omega_1 a)}{K_0(\omega_1 a)}\right]^{1/2} \tag{88}$$

Equation (87) is evaluated in the same manner as before. Omitting details of the derivation, the complete solution was found to be

$$c_m(z, t) = \tfrac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp\left(\frac{v_m z}{2D_m} - z_p z\right) \cdot \sin\left(\frac{\lambda^2 D_a t}{a^2 R_a} - z_m z\right)\frac{d\lambda}{\lambda} \tag{89}$$

where

$$z_p = [\tfrac{1}{2}(r_p + \Omega_1)]^{1/2} \qquad z_m = [\tfrac{1}{2}(r_p - \Omega_1)]^{1/2} \tag{90a}$$

$$r_p = (\Omega_1^2 + \Omega_2^2)^{1/2} \tag{90b}$$

$$\Omega_1 = \frac{v_m^2}{4D_m^2} + \frac{2\theta_a D_a\lambda A_1^0}{a^2 D_m\theta_f} \tag{90c}$$

$$\Omega_2 = \frac{R_m D_a\lambda^2}{a^2 R_a D_m} + \frac{2\theta_a D_a\lambda A_2^0}{a^2 D_m\theta_f} \tag{90d}$$

$$A_1^0 = -\frac{\mathrm{Ker}(\lambda)\,\mathrm{Ker}'(\lambda) + \mathrm{Kei}(\lambda)\,\mathrm{Kei}'(\lambda)}{\mathrm{Ker}^2(\lambda) + \mathrm{Kei}^2(\lambda)} \tag{90e}$$

$$A_2^0 = \frac{\mathrm{Kei}(\lambda)\,\mathrm{Ker}'(\lambda) - \mathrm{Ker}(\lambda)\,\mathrm{Kei}'(\lambda)}{\mathrm{Ker}^2(\lambda) + \mathrm{Kei}^2(\lambda)} \tag{90f}$$

Note that the solution above has the same structure as the solution for the finite cylindrical soil mantle ((71) and related equations).

Approximate Solutions for No Dispersion

When longitudinal dispersion in the macropore region is neglected ($D_m \to 0$), and when again only a single macropore in a radially infinite soil system is considered, the Laplace transform solution for $\bar{c}_m$ is

$$\bar{c}_m(z, s) = \frac{1}{s}\exp\left[-\frac{R_m s z}{v_m} - \frac{2z\theta_a(D_a R_a s)^{1/2}}{a\theta_f v_m}\frac{K_1(\omega_1 a)}{K_0(\omega_1 a)}\right] \tag{91}$$

which, when inverted, yields for $t > R_m z/v_m$

$$c_m(z, t) = \frac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp\left(-\frac{2\theta_a D_a\lambda z A_1^0}{a^2\theta_f v_m}\right) \cdot \sin\left[\frac{\lambda^2 D_a(v_m t - R_m z)}{a^2 R_a v_m} - \frac{2\theta_a D_a z\lambda A_2^0}{a^2\theta_f v_m}\right]\frac{d\lambda}{\lambda} \tag{92}$$

where A_1^0 and A_2^0 are given by (90*e*) and (90*f*). Equation (92) is not much simpler than the other solutions, and hence there is little reason to neglect dispersion if the only purpose is to simplify the mathematics. However, a useful approximate solution valid for small values of time can be obtained by suitably approximating the modified Bessel functions K_1 and K_0 in (91). Using asymptotic expansions for K_1 and K_0 valid for large values of s (e.g., those given by *McLachlan* [1961, p. 221]), one can show that the ratio of the two Bessel functions can be approximated by the series

$$\frac{K_1(x)}{K_0(x)} = 1 + \frac{1}{2x} - \frac{1}{8x^2} + \frac{1}{8x^3} + \cdots \tag{93}$$

Using only two terms of this series, (91) reduces to

$$\bar{c}_m(z, s) = \frac{1}{s}\exp\left[-\frac{zR_m s}{v_m} - \frac{2z\theta_a(D_a R_a s)^{1/2}}{a\theta_f v_m} - \frac{z\theta_a D_a}{a^2\theta_f v_m}\right] \tag{94}$$

which yields the following approximate solution for c_m:

$$c_m(z, t) = 0 \qquad v_m t \le R_m z$$

$$c_m(z, t) = \exp\left(-\frac{\theta_a D_a z}{a^2\theta_f v_m}\right)\mathrm{erfc}\left[\frac{\theta_a z}{a\theta_f v_m}\left(\frac{D_a R_a}{t - R_m z/v_m}\right)^{1/2}\right] \qquad v_m t > R_m z \tag{95}$$

Equation (95) has a form that is very similar to an exact solution used recently by *Grisak and Pickens* [1981] to calculate concentration distributions along a planar void in a fractured medium.

The above method for approximating c_m can also be extended to obtain an estimate for the soil matrix concentration c_a, the Laplace transform of which was given by (83). To do this, $K_0(x)$ for large values of x was approximated by the series (see, for example, *Olver* [1970, equation 9.7.2.])

$$K_0(x) = \left(\frac{\pi}{2x}\right)^{1/2} e^{-x}\left(1 - \frac{1}{8x} + \frac{9}{128x^2} - \frac{75}{1024x^3} + \cdots\right) \tag{96}$$

Substituting (96) into (83), carrying out the division, and retaining four terms leads to

$$\bar{c}_a = \bar{c}_m \left(\frac{a}{r}\right)^{1/2} \exp\left[-(r-a)\left(\frac{R_a s}{D_a}\right)^{1/2}\right] \cdot \left(1 + \frac{P_1}{s^{1/2}} + \frac{P_2}{s} + \frac{P_3}{ss^{1/2}}\right) \tag{97}$$

where

$$P_1 = \frac{(D_a)^{1/2}}{8a(R_a)^{1/2}}\left(1 - \frac{a}{r}\right)$$

$$P_2 = \frac{D_a}{128a^2R_a}\left(-7 - \frac{2a}{r} + \frac{9a^2}{r^2}\right) \tag{98}$$

$$P_3 = \frac{(D_a)^{3/2}}{1024a^3(R_a)^{3/2}}\left(59 + \frac{7a}{r} + \frac{9a^2}{r^2} - \frac{75a^3}{r^3}\right)$$

Substituting (94) into (97) gives

$$\bar{c}_a = \left(\frac{a}{r}\right)^{1/2} \exp\left(-\frac{zR_m s}{v_m} - \frac{z\theta_a D_a}{a^2\theta_f v_m} - \eta s^{1/2}\right) \cdot \left(\frac{1}{s} + \frac{P_1}{s^{3/2}} + \frac{P_2}{s^2} + \frac{P_3}{s^{5/2}}\right) \tag{99}$$

where

$$\eta = \frac{2z\theta_a(D_aR_a)^{1/2}}{a\theta_f v_m} + (r-a)\left(\frac{R_a}{D_a}\right)^{1/2} \tag{100}$$

Finally, inverting (100) gives the following approximate solution for the soil matrix concentration c_a:

$$c_a(z, r, t) = 0 \qquad t_1 \le 0$$

$$c_a(z, r, t) = \left(\frac{a}{r}\right)^{1/2} \exp\left(-\frac{\theta_a D_a z}{a^2\theta_f v_m}\right)\left\{[2P_1 - \eta P_2 + \tfrac{1}{3}(4t_1 + \eta^2)P_3] \exp\left(-\frac{\eta^2}{4t_1}\right) + \left[1 - \eta P_1 + \left(t_1 + \frac{\eta^2}{2}\right)P_2 - \eta \cdot \left(t_1 + \frac{\eta^2}{6}\right)P_3\right] \operatorname{erfc}\left(\frac{\eta}{2(t_1)^{1/2}}\right)\right\} \qquad t_1 > 0 \tag{101}$$

where

$$t_1 = t - (zR_m/v_m) \tag{102}$$

As with (95), (101) applies only when dispersion in the macropore system is neglected and when the radial soil matrix surrounding the cylindrical macropore extends to infinity. In addition, the approximate solutions are valid only for small values of time. Numerical experimentation with (101) indicated that this equation gives accurate results for the following condition:

$$D_a t_1/a^2 R_a < 0.5 \tag{103}$$

However, the solution diverges quickly when this condition is not satisfied anymore. It was found also that little accuracy is lost when the higher-order terms containing P_1, P_2, and P_3 in (97) are neglected. In that case, (101) becomes simply

$$c_a(z, r, t) = 0 \qquad t \le t_1$$

$$c_a(z, r, t) = \left(\frac{a}{r}\right)^{1/2} \exp\left(-\frac{z\theta_a D_a}{a^2 v_m \theta_f}\right) \operatorname{erfc}\left(\frac{\eta}{2(t_1)^{1/2}}\right) \qquad t_1 > 0 \tag{104}$$

Because of fewer approximations in its derivation, (95) has a much broader range of application than either (101) or (104). Some results illustrating the accuracy and applicability of the approximate solutions are given later.

Numerical Implementation

Numerical integration techniques were used to evaluate the integrals of (71), (75), and similar equations in this study. The integrands of these integrals consist of the product of a decaying exponential function and a rapidly oscillating sinusoidal-shaped function, either a sine wave (equation (71)) or a similar oscillating function (equation (75)). Because of the generally rapid oscillatory behavior of the integrands as a function of the integration parameter λ, direct numerical evaluation of the complete integrals using Gaussian quadrature techniques often leads to inaccurate results, even with an excessive number of integration points. Except for minor differences in implementation, our method for evaluating the integrals was the same as that used by *Rasmuson and Neretnieks* [1981] for similar expressions dealing with radionuclide transport between and into spherical aggregates. In summary, each infinite integral is first replaced by a finite series of finite integrals (I_i) as follows:

$$c_m = \tfrac{1}{2} + \sum_{i=1}^{n} I_i \tag{105}$$

with

$$I_i = \int_{\lambda_i}^{\lambda_{i+1}} f(\lambda)\, d\lambda \tag{106}$$

where $f(\lambda)$ represents the integrand, $\lambda_1 = 0$, and λ_i $(i > 1)$ are consecutive positive roots of the integrand. The number of terms n in (104) could be limited because of two considerations. First, n was chosen such that λ_{n+1} is the first root for which the exponential part of $f(\lambda)$ becomes less than exp (−20). Second, the number of terms could be limited greatly by repeatedly averaging the partial sums of (105). By means of an example, *Rasmuson and Neretnieks* [1981] showed that this method is extremely accurate and very efficient when $f(\lambda)$ oscillates rapidly and numerous terms otherwise would have been required to reach convergence. We refer to the paper by Rasmuson and Neretnieks for a more detailed discussion of this method using repeated averaging. Using this method, the number of terms for most of our calculations could be limited to only 10, leading to answers that have an accuracy of at least three significant digits.

Crucial to a correct evaluation of the analytical solutions are accurate approximations of the modified Bessel functions (K_0, I_0, K_1, etc.) and the different Kelvin functions (Ber, Ker, etc.). For our calculations we used the polynomial approximations of these functions as listed by *Olver* [1970]. In addition, several simplified expressions for various terms in $A_1{}^0$ and $A_2{}^0$ (equations (90*e*) and (90*f*)) were derived:

$$\mathrm{Ker}^2(\lambda) + \mathrm{Kei}^2(\lambda) = \alpha^2 + \frac{\pi^2}{16} - \frac{\pi\lambda^2}{8} + \frac{\lambda^4}{512} \cdot (\pi^2 + 40\alpha + 16\alpha^2 + 32) - \frac{\pi\lambda^6}{1728} \quad (107a)$$

$$\mathrm{Ker}(\lambda)\,\mathrm{Ker}'(\lambda) + \mathrm{Kei}(\lambda)\,\mathrm{Kei}'(\lambda) = -\frac{\alpha}{x} - \frac{\pi\lambda}{8} + \frac{\lambda^3}{256}(\pi^2 + 32\alpha + 16\alpha^2 + 22) - \frac{\pi\lambda^5}{576} \quad (107b)$$

$$\mathrm{Kei}(\lambda)\,\mathrm{Ker}'(\lambda) - \mathrm{Ker}(\lambda)\,\mathrm{Kei}'(\lambda) = \frac{\pi}{4\lambda} - \frac{\lambda}{32} \cdot (\pi^2 + 8 + 16\alpha + 16\alpha^2) + \frac{\pi\lambda^3}{32} - \frac{\lambda^5}{27{,}648}(9\pi^2 + 356 + 408\alpha + 144\alpha^2) \quad (107c)$$

where

$$\alpha = \ln(2/\lambda) - 0.57721566 \quad (108)$$

(the last term of (108) is Euler's constant). Use of the above expressions leads to an accuracy of at least five significant digits in $A_1{}^0$ and $A_2{}^0$ when λ is less than 0.5. For $\lambda > 3$, the following approximations have a relative error of less than 10^{-5}:

$$A_1{}^0(\lambda) = \frac{1}{2^{1/2}}(1 + 8y - 16y^2 + 3136y^4) \quad (109a)$$

$$y = \frac{2^{1/2}}{16\lambda}$$

$$A_2{}^0(\lambda) = \frac{1}{2^{1/2}}(1 + 16y^2 - 254y^3 + 3204y^4) \quad (109b)$$

Finally, for relatively large values of ζ_0 and/or λ, A_1 and A_2 are closely approximated by

$$A_1(\lambda) \sim 2^{1/2}A_1{}^0(\lambda) \qquad A_2(\lambda) \sim 2^{1/2}A_2{}^0(\lambda) \quad (110)$$

The relative error in these approximations is less than 10^{-5} for $\zeta_0\lambda > 10$. These last approximations were expected, since the solution for the radially infinite soil matrix (equation (89)) forms a limiting case of the solution for the finite soil matrix (equation (71)) when $\zeta_0 \to \infty$. This can be demonstrated by writing (71) and the related expressions of this solution in terms of the original parameters. Using (26)–(29) and the definitions of θ_m and θ_{im} as indicated by (2) and (3), one can express the solution for the radially finite soil matrix also in the form of (89), (90*a*), and (90*b*), provided that Ω_1 and Ω_2 are given by

$$\Omega_1 = \frac{v_m{}^2}{4D_m{}^2} + \frac{2^{1/2}\theta_a D_a \lambda A_1}{a^2 D_m \theta_f} \quad (111a)$$

$$\Omega_2 = \frac{R_m D_a \lambda^2}{a^2 R_a D_m} + \frac{2^{1/2} D_a \theta_a \lambda A_2}{a^2 D_m \theta_f} \quad (111b)$$

For the limiting case when $\zeta_0 \to \infty$ ($b \to \infty$), these equations should reduce to (90*c*) and (90*d*), thus validating the approximations given by (110).

EXAMPLE

The exact and approximate solutions presented in this study deal with solute transport through large cylindrical macropores with simultaneous diffusional exchange of material between the macropores and the adjacent soil matrix. Conceptually similar analytical solutions for macropore transport with simultaneous matrix diffusion were presented earlier by *Rasmuson and Neretnieks* [1981] for solute transport between spherical aggregates, by *Pellett* [1966] for transport between solid cylindrical structures, and by *Tang et al.* [1981], *Grisak and Pickens* [1981], and *Sudicky and Frind* [1982] for movement through rectangular voids. Calculated solute distributions presented in those papers clearly demonstrate the important effects of various system parameters (v_m, D_m, D_a, aggregate size, and void width) on solute transport. Although our study deals with different soil structures, qualitatively similar effects of various system parameters on transport can be demonstrated also for cylindrical macropores. It should be noted that a number of sensitivity analyses for the closely related mobile-immobile type transport models have been documented also, notably by *Villermaux and van Swaaij* [1969], *Thackston and Schnelle* [1970], *van Genuchten and Wierenga* [1976], *Vachaud et al.* [1976], and *van Genuchten and Cleary* [1979]. Consequently, we will not duplicate previously published discussions of the effects of various parameters on transport; the reader is referred to the other papers for such a discussion. Instead, only one example will be given here to illustrate the effects of neglecting dispersion in the macropore region and also of assuming a radially infinite rather than finite soil matrix surrounding the macropore.

Figure 2 shows calculated breakthrough curves for a 40.4-cm-long porous column that contains a straight cylindrical macropore of radius 0.073 cm. Except for an estimate for the dispersion coefficient, all parameter values used for this example are the same as those determined experimentally by *De Cockborne* [1980] in a study of nitrate movement through artificially constructed laboratory soil columns. These experiments, along with a number of theoretical predictions, will be discussed in a forthcoming paper. While the effect of dispersion on the general shape of the curve is clearly visible at early times, Figure 2 shows that at later times it is extremely small or nonexistent. For this example, an arbi-

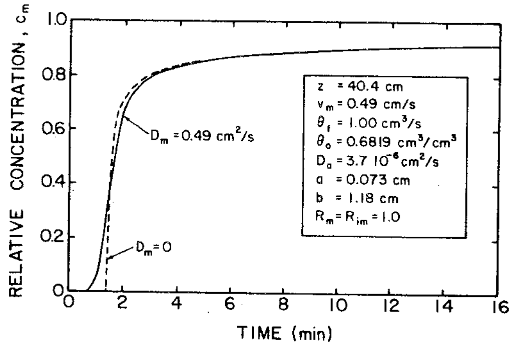

Fig. 2. Calculated breakthrough curves for nitrate movement through a 40.4-cm-long porous medium containing a straight cylindrical macropore.

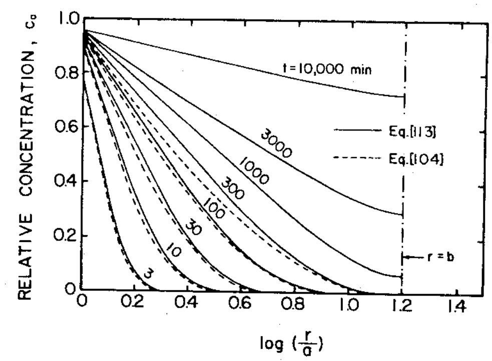

Fig. 3. Radial concentration distributions at $z = 40.4$ cm for different values of t.

trary value of 1 cm for the dispersivity was assumed, thus making the dispersion coefficient numerically equal to the macropore water velocity (see Figure 2). This value of 1 cm is somewhat less than the 4 cm used by *Grisak and Pickens* [1980*b*, Figure 8] to describe chloride breakthrough data through fractured clayey till material.

Approximate solution (95) was found to generate essentially the same results as the solution for negligible dispersion in the macropore region (i.e., the same as the dashed curve in Figure 2). Some small deviations of the order of about 0.01 to 0.03 relative concentration units between the approximate solution and the exact solution for a radially infinite soil matrix were present between $t = 50$ and $t = 20{,}000$ min. Therefore approximate solution (95) provides a simple, accurate, and extremely useful tool for studying solute transport through cylindrical macropores.

The exact solutions for a finite ($b = 1.18$ cm) and an infinite ($b \to \infty$) soil matrix were found to generate exactly the same breakthrough curves until t reached a value of about 500 min (results given by the solid curve in Figure 2). This duplication of the results could have been expected also when considering the radial concentration distribution in the soil matrix, plotted in Figure 3 for various values of t. The dashed curves in this figure were calculated with the approximate solution discussed earlier (equation (104)), whereas the solid curves were obtained with an alternative approximate solution that will be discussed later. Figure 3 clearly shows that no influence of the outer boundary at $r = b$ on the radial concentration profiles is present until t reaches a value of about 500 min. Hence similar effects of the outer boundary on solute distributions in the macropore should not be present until that time.

From Figure 2 it is evident that the shape of the breakthrough curve for no dispersion is roughly that of a step function, being zero until $t = t_1$ while for $t > t_1$ the concentration remains fairly constant at about 0.9 as predicted with (95). If we assume that $c_m(z, t)$ indeed remains constant for $t > t_1$, then we can use this information to fix boundary condition (81*a*) and solve the radial diffusion equation for the soil matrix without having to consider the direct coupling of that equation with the transport equation for the macropore system. Thus the problem becomes to solve (80) subject to (81*b*) and the condition

$$c_a(z, a, t) = 0 \qquad t \le t_1$$
$$c_a(z, a, t) = c_m^{\,0}(z, t) \qquad t > t_1 \qquad (112)$$

where $c_m^{\,0}(z, t)$ is given by (95) and further assumed to be a constant in the solution process. The solution of this problem is

$$c_a(z, r, t) = 0 \qquad t \le t_1$$
$$c_a(z, r, t) = c_m^{\,0}(z, t)B(r, t_1) \qquad t > t_1 \qquad (113)$$

where

$$B(r, t_1) = 1 - \pi \sum_{n=1}^{\infty} \exp\,(-\,D_a\alpha_n^2 t_1/R_a) J_1^2(\alpha_n b)$$
$$\cdot \left[\frac{J_0(\alpha_n r)Y_0(\alpha_n a) - Y_0(\alpha_n r)J_0(\alpha_n a)}{J_1^2(\alpha_n b) - J_0^2(\alpha_n a)} \right] \qquad (114)$$

and where α_n are the roots of

$$J_0(\alpha_n a)Y_1(\alpha_n b) - J_1(\alpha_n b)Y_0(\alpha_n a) = 0 \qquad (115)$$

Hence (113) describes radial diffusion from a hollow cylindrical pore into a finite soil mantle, subject to a constant boundary condition imposed at the pore wall. The solution given here is a simplification of a more general solution given by *Crank* [1956, p. 80].

The solid curves in Figure 3 were obtained with (113) while using (95) for $c_m^{\,0}(z, t)$. Note that for small times this solution generates approximately the same results as the much simpler solution (104); this verifies the applicability and relative accuracy of (113). For times greater than about 30 min, (104) becomes invalid, and only (113) can be used to obtain estimates for the radial concentration distribution $c_a(z$ $r, t)$. Rather than (95), one of the more complete solutions (71), (75), or (92) could have been used also for $c_m^{\,0}(z, t)$ in (113). However, this will not lead to significantly different answers, at least for the parameter values used here. It should be noted that the series solution (113) requires a large number of terms when t is small. For example, about 10 to 40 terms are needed to obtain an accuracy of about 0.001 concentration units when t is less than 30 min in our example. For $t > 100$, however, only one to three terms of the series are required.

SUMMARY AND CONCLUSIONS

This paper presents several exact and approximate solutions of the equations describing convective-dispersive solute transport through large cylindrical macropores with simultaneous radial diffusion from the macropore liquid phase into the surrounding soil matrix. Analytical solutions are presented for both a radially finite and a radially infinite soil matrix. By means of an example, it is shown that at early times little accuracy is lost when the radially finite soil mantle is replaced by an infinite system. For at least one set of system parameters, a simple approximate solution for the concentration in the macropore liquid phase was found to give an excellent approximation of the more complicated exact solution. This approximate solution ignores dispersion in the macropore system and also assumes that the soil matrix surrounding the macropore extends to infinity.

All exact solutions given in this paper pertain to concentration distributions in the macropore system. In addition, two approximate solutions are given that can be used to estimate temporal and radial concentration distribution within the soil matrix itself.

NOTATION

a radius of cylindrical macropore.
A_1, A_2 see (65*c*) and (65*d*).
A_1^0, A_2^0 see (90*e*) and (90*f*).
b outer radius of soil mantle surrounding macropore.
Ber_ν, Bei_ν, Ber_ν', Bei_ν' Kelvin functions ($\nu = 0, 1$).
B see (114).
c_a relative concentration of soil matrix liquid phase.
c_{im} average relative concentration of soil matrix liquid phase.
c_m relative concentration of macropore liquid phase.
c_{m1}, c_{m3} analytical solutions of c_m for first- and third-type input boundary conditions, respectively.
$\bar{c}_a$, $\bar{c}_{im}$, $\bar{c}_m$ Laplace transforms of c_a, c_{im}, and c_m, respectively.
C_1, C_2 constants in (41).
C_0, C_i input and initial concentrations, respectively.
C_a local concentration of soil matrix liquid phase.
C_{im} average concentration of soil matrix liquid phase.
C_m concentration of macropore liquid phase.
D_a soil matrix molecular or ionic diffusion coefficient.
D_m dispersion coefficient of macropore region.
f_m mass fraction of all adsorption sites associated with the macropore region.
I_0, I_1 modified Bessel functions.
I_i see (106).
J_0, J_1 Bessel function of the first kind.
k average distribution coefficient of soil system.
k_a distribution coefficient for bulk soil matrix.
Ker_ν, Kei_ν, Ker_ν', Kei_ν' Kelvin functions ($\nu = 0, 1$).
k_m, k_{im} distribution coefficients for mobile and immobile regions, respectively.
K_0, K_1 modified Bessel functions.
L column length or profile depth.
M, N see (46*a*) and (46*b*).
M_1, M_2 see (61*a*) and (61*b*).
n number of terms in (105).
N_1, N_2 see (63*a*) and (63*b*).
n_p number of macropores per unit cross-sectional area.
P_1, P_2, P_3 see (98).
P_m column Peclet number.
q volumetric flux density.
r radial coordinate.
r_p see (67*a*).
R total retardation factor.
R_a, R_{im} retardation factors for bulk soil matrix.
R_m retardation factor of macropore region.
s Laplace transform variable.
S_a, S_{im} local and average adsorbed concentration of bulk soil matrix, respectively.
S_m adsorbed concentration of macropore region.
t time.
t_1 adjusted time (see (102)).
T dimensionless time (pore volume).
v_m average fluid velocity through macropores.
V_a, V_f volume fractions of macropore and micropore regions.
x dummy variable.
y integration variable.
Y_0, Y_1 Bessel functions of the second kind.
z distance.
z_m, z_p see (72*a*) and (72*b*).
$Z = z/L$.
α see (108).
α_n roots of (115).
β see (29*a*).
γ see (29*b*).
ε limiting constant in (54).
$\zeta = r/a$.
$\zeta_0 = b/a$.
η see (100).
θ total volumetric water content, equal to $\theta_m + \theta_{im}$.
θ_m, θ_{im} mobile and immobile water contents, respectively.
θ_a, θ_f local volumetric water contents of the micropore and macropore regions, respectively.
λ integration variable.
λ_i values of λ for which the integrands of (71), (75), or (98) become zero ($\lambda_1 = 0$).
ρ soil bulk density.
ρ_a, ρ_f local bulk densities of the micropore and macropore regions, respectively.
ρ_m, ρ_{im} see (13).
σ_n roots of (53).
τ integration variable.
ϕ_m, ϕ_{im} see (4).
Φ see (88).
ω see (42).
ω_1 see (84).
Ω see (50).
Ω_1, Ω_2 see (65*a*) and (65*b*) or (90*c*) and (90*d*).

REFERENCES

Baker, L. E., Effects of dispersion and dead-end pore volume in miscible flooding, *Soc. Pet. Eng. J.*, *17*, 219–227, 1977.

Bennett, A., and F. Goodridge, Hydrodynamic and mass transfer studies in packed absorption columns, *Trans. Inst. Chem. Eng.*, *48*, 232–244, 1970.

Beven, K., and P. Germann, Macropores and water flow in soils, *Water Resour. Res.*, *18*(5), 1311–1325, 1982.

Bouma, J., Soil morphology and preferential flow along macropores, *Agric. Water Manage.*, *3*, 235–250, 1981.

Brigham, W. E., Mixing equations in short laboratory cores, *Soc. Pet. Eng. J.*, *14*, 91–99, 1974.

Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed., 510 pp., Oxford University Press, New York, 1959.

Coats, K. H., and B. D. Smith, Dead end pore volume and dispersion in porous media, *Soc. Pet. Eng. J., 4,* 73–84, 1964.

Crank, J., *The Mathematics of Diffusion*, 347 pp., Oxford University Press, New York, 1956.

Davidson, J. M., P. S. C. Rao, R. E. Green, and H. M. Selim, Evaluation of conceptual models for solute behavior in soil-water systems, in *Agrochemicals in Soils*, edited by A. Banin and U. Kafkafi, pp. 241–251, Pergamon, New York, 1980.

De Cockborne, A., Transfert des nitrates, en milieu poreux saturé en présence d'une porosité structurale, 92 pp., thesis, Univ. Sci. et Méd. de Grenoble, France, 1980.

Drummond, J. E., and A. McNabb, The heating of cold-water intrusions in a geothermal field, *New Zealand J. Sci., 14,* 665–672, 1972.

Freeze, R. A., and J. A. Cherry, *Groundwater*, 604 pp., Prentice-Hall, Englewood Cliffs, N. J., 1979.

Gaudet, J. P., H. Jégat, G. Vachaud, and P. Wierenga, Solute transfer with exchange between mobile and stagnant water through unsaturated sand, *Soil Sci. Soc. Am. J., 41,* 665–671, 1977.

Grisak, G. E., and J. F. Pickens, Solute transport through fractured media, 1, The effect of matrix diffusion, *Water Resour. Res., 16*(4), 719–730, 1980*a*.

Grisak, G. E., and J. F. Pickens, Solute transport through fractured media, 2, Column study of fractured till, *Water Resour. Res., 16*(4), 731–739, 1980*b*.

Grisak, G. E., and J. F. Pickens, An analytical solution for solute transport through fractured media with matrix diffusion, *J. Hydrol., 52,* 47–57, 1981.

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

McLachlan, N. W., *Bessel Functions for Engineers*, 2nd ed., 239 pp., Oxford University Press, New York, 1961.

Olver, F. W. J., Bessel functions of integer order, in *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. Stegun, pp. 355–433, Dover, New York, 1970.

Passioura, J. B., Hydrodynamic dispersion in aggregated media, I, Theory, *Soil Sci., 111*(6), 339–344, 1971.

Pellett, G. L., Longitudinal dispersion, intraparticle diffusion, and liquid-phase mass transfer during flow through multiparticle systems, *Tappi, 49,* 75–82, 1966.

Rao, P. S. C., J. M. Davidson, R. E. Jessup, and H. M. Selim, Evaluation of conceptual models for describing non-equilibrium adsorption-desorption of pesticides during steady flow in soils, *Soil Sci. Soc. Am. J., 43*(1), 22–28, 1979.

Rao, P. S. C., R. E. Jessup, D. E. Rolston, J. M. Davidson, and D. P. Kilcrease, Experimental and mathematical description of non-adsorbed solute transfer by diffusion in spherical aggregates, *Soil Sci. Soc. Am. J., 44,* 684–688, 1980*a*.

Rao, P. S. C., D. E. Rolston, R. E. Jessup, and J. M. Davidson, Solute transport in aggregated porous media: Theoretical and experimental evaluation, *Soil Sci. Soc. Am. J., 44,* 1139–1146, 1980*b*.

Rasmuson, A., and I. Neretnieks, Exact solution for diffusion in particles and longitudinal dispersion in packed beds, *AIChE J., 26,* 686–690, 1980.

Rasmuson, A., and I. Neretnieks, Migration of radionuclides in fissured rock: The influence of micropore diffusion and longitudinal dispersion, *J. Geophys. Res., 86*(B5), 3749–3758, 1981.

Rosen, J. B., Kinetics of a fixed bed system for solid diffusion into spherical particles, *J. Chem. Phys., 20*(3), 387–394, 1952.

Scotter, D. R., Preferential solute movement through large soil voids, I, Some computations using simple theory, *Aust. J. Soil Res., 16,* 257–267, 1978.

Skopp, J., and A. W. Warrick, A two-phase model for the miscible displacement of reactive solutes in soil, *Soil Sci. Soc. Am. J., 38*(4), 545–550, 1974.

Skopp, J., W. R. Gardner, and E. J. Tyler, Solute movement in structured soils: Two-region model with small interaction, *Soil Sci. Soc. Am. J., 45,* 837–842, 1981.

Sudicky, E. A., and E. O. Frind, Contaminant transport in fractured porous media: Analytical solutions for a system of parallel fractures, *Water Resour. Res., 18*(6), 1634–1642, 1982.

Tang, D. H., E. O. Frind, and E. A. Sudicky, Contaminant transport in fractured porous media: Analytical solution for a single fracture, *Water Resour. Res., 17*(3), 555–564, 1981.

Thackston, E. L., and K. B. Schnelle, Jr., Predicting effects of dead zones on stream mixing, *J. Environ. Eng. Div. Am. Soc. Civ. Eng., 96*(SA2), 319–331, 1970.

Thomas, G. W., and R. E. Phillips, Consequences of water movement in macropores, *J. Environ. Qual., 8*(2), 149–152, 1979.

Vachaud, G., P. J. Wierenga, J. P. Gaudet, and H. Jegat, Simulation of miscible displacement in unsaturated porous media, in *System Simulation in Water Resources,* edited by G. C. Vansteenkiste, pp. 129–140, North-Holland, New York, 1976.

van Genuchten, M. T., Non-equilibrium transport parameters from miscible displacement experiments, 88 pp., *Res. Rep. 119,* U.S. Salinity Lab., U.S. Dep. of Agric./Sci. and Educ. Admin., Riverside, Calif., 1981.

van Genuchten, M. T., and R. W. Cleary, Movement of solutes in soil: Computer-simulated and laboratory results, in *Soil Chemistry,* vol. B, *Physico-Chemical Models,* edited by G. H. Bolt, pp. 349–386, Elsevier, New York, 1979.

van Genuchten, M. T., and P. J. Wierenga, Mass transfer studies in sorbing porous media, I, Analytical solutions, *Soil Sci. Soc. Am. J., 40*(4), 473–480, 1976.

Villermaux, J., and W. P. M. van Swaaij, Modèle représentatif de la distribution des temps de séjour dans un réacteur semi-infini à dispersion axiale avec zones stagnantes. Application à l'écoulement ruisselant des colonnes d'anneaux Raschig, *Chem. Eng. Sci., 24,* 1097–1111, 1969.

Wierenga, P. J., Solute transport through soils: Mobile-immobile water concepts, Proceedings of the Symposium on Unsaturated Flow and Transport Modeling, March 22–23, Seattle, Washington, *Rep. NUREG/CP-0030,* edited by E. M. Arnold, G. W. Gee, and R. W. Nelson, pp. 211–226, Pacific Northwest Laboratory, Richland, Wash., 1982.

R. Guennelon, Centre de Recherches Agronomiques d'Avignon, I.N.R.A., B.P. 91, 84140 Montfavet, France.

D. H. Tang, Exxon Production Research Company, P. O. Box 2189, Houston, TX 77001.

M. T. van Genuchten, U.S. Salinity Laboratory, 4500 Glenwood Drive, Riverside, CA 92501.

(Received August 16, 1983;
revised November 10, 1983;
accepted November 18, 1983.)