9 1 4

Geoderma, 38 (1986) 165—183 165
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

MODELS FOR SIMULATING SALT MOVEMENT IN AGGREGATED FIELD SOILS

M.Th. VAN GENUCHTEN and F.N. DALTON

U.S. Salinity Laboratory, USDA—ARS, Riverside, Calif. (U.S.A.)

(Accepted for publication February 28, 1986)

ABSTRACT

Van Genuchten, M.Th. and Dalton, F.N., 1986. Models for simulating salt movement in aggregated field soils. Geoderma, 38: 165—183.

This paper reviews several "two-region" type models for simulating salt movement in aggregated soils. A common feature of these models is the assumption that solutes are transported by convection and dispersion through well-defined pores or cracks, while diffusion-type equations are used to describe solute transfer inside the soil micropores. Analytical solutions are currently available for several aggregate shapes (spherical, cylindrical and line-sheet type aggregates). A recently developed transformation extends the two-region modeling approach to more general conditions involving aggregates of arbitrary geometry. The method is based on the replacement of a given aggregated soil by a reference soil made up of uniformly-sized spherical aggregates with the same average diffusion properties as the original soil. The method can also be used to quantify the mass transfer coefficient in a first-order rate model for solute exchange between mobile and immobile liquid zones. An advantage of the first-order approach is that it can be included easily in relatively simple management-oriented models using parameters that can be given a physical interpretation. This paper also presents several previously unpublished expressions that lump the effects of intra-aggregate diffusion into an effective dispersion coefficient for use in the classical two-parameter equilibrium transport equation.

INTRODUCTION

The efficiency of applied fertilizers and pesticides in the field, the leaching efficiency of salt-affected soils, and concern for soil and groundwater pollution in general have motivated numerous theoretical and experimental studies on solute transport. Most theoretical studies in the past have focused on transport processes in repacked laboratory soil columns or in relatively uniform field soils. Transport in such soils during steady-state flow is generally predicted well with the classical convection—dispersion solute transport equation:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} \tag{1}$$

0016-7061/86/$03.50

where c = solution concentration, v = average pore water velocity, D = dispersion coefficient, R = retardation factor (for linear equilibrium adsorption/exchange), t = time, and z = distance.

It is now generally recognized that information based on eq. 1 is of limited value when dealing with aggregated soils, especially during but not necessarily limited to saturated flow conditions. Field soils usually are structured in some way by containing large continuous macropores, such as drying cracks, earthworm channels, gopher holes, decayed root channels, or interpedal voids in naturally aggregated soils (fig. 1). The presence of macropores causes surface-applied chemicals to move rapidly through the soil profile, thus by-passing interactions with much of the soil matrix. The result is a lower application efficiency for fertilizers and pesticides and/or an increased potential for pollution of underlying groundwater systems. Because of the bypassing process, desalination of initially saline soils will similarly require much more water than would be predicted on the basis of eq. 1. Much information has been gathered over the last few years that clearly demonstrates this bypassing process, alternatively termed incomplete or partial mixing, short-circuiting, and non-Fickian transport. Recent reviews of experimental evidence are given by Thomas and Philips (1979), Bouma (1981), Wierenga (1982) and White (1985).

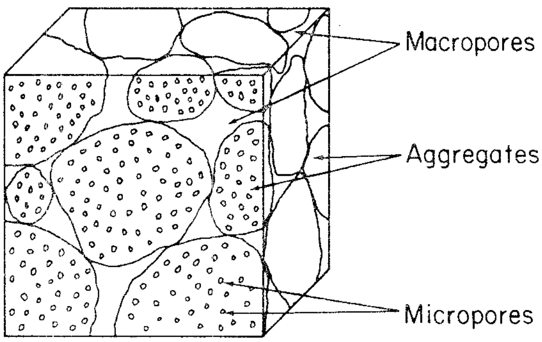

Fig. 1. Schematic picture of an aggregated soil.

Attempts to improve solute transport predictions in aggregated soils have resulted in two-region or bicontinuum transport models that consider a bimodal pore-water velocity distribution: water inside the aggregates is assumed to be stagnant (non-flowing or immobile) while water in the larger interaggregate pores is considered to be highly mobile. Solute transfer between the two liquid phases is assumed to be a diffusion controlled process and described by either a semi-empirical first-order rate expression (Coats and Smith, 1964; van Genuchten and Wierenga, 1976), or by Fick's diffusion law if the geometry of the aggregates can be specified explicitly (Rasmuson and Neretnieks, 1980; Tang et al., 1981).

This paper reviews several of these two-region type transport models, notably those for which analytical solutions exist. Briefly discussed is a recently proposed scaling method (van Genuchten, 1985) for transforming soil aggregates of known geometry into uniformly-sized spherical aggregates with approximately the same diffusion properties as the original aggregates. A similar transformation is also used to obtain a physical basis for the mass transfer coefficient that appears in a first-order rate model describing solute exchange between mobile (interaggregate) and immobile (intra-aggregate) regions (van Genuchten and Wierenga, 1976). Following a method previously used by Raats (1981), expressions are derived that lump the effects of intra-aggregate diffusion into an equivalent dispersion coefficient for use in eq. 1. Results are consistent with equations obtained earlier by Passioura (1971), Bolt (1979) and Valocchi (1985) using alternative methods.

FIRST-ORDER TYPE TWO-REGION TRANSPORT MODELS

A relatively simple two-region model results when a first-order rate expression is used to describe solute transfer between the mobile (inter-aggregate) and immobile (intra-aggregate) liquid phases. Using the notation of van Genuchten and Wierenga (1976), the following coupled set of equations can be shown to apply:

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

$$\theta_{im} R_{im} \frac{\partial c_{im}}{\partial t} = \alpha(c_m - c_{im}) \tag{3}$$

where the subscripts m and im refer to the mobile and immobile regions of the soil respectively, and where α is a first-order mass transfer coefficient describing diffusional exchange between the inter- and intra-aggregate liquid phases. The model assumes that this exchange occurs at a rate proportional to the concentration difference between the two liquid phases. Volumetric water contents θ_m and θ_{im} are defined such that $\theta = \theta_m + \theta_{im}$ is the total water content of the system. We will refer to eqs. 2 and 3 as the first-order rate (FO) model.

Mathematically it is convenient to put the FO model, and all other models discussed in this paper, in dimensionless form. Table I summarizes the different models in terms of the dimensionless variables listed in Table II. In the latter table, T represents the number of pore volumes leached through a soil profile or column of arbitrary length L, q is the volumetric fluid flux density ($q = \theta v = \theta_m v_m$), whereas P and P_m represent Peclet numbers. The dimensionless coefficient β accounts not only for the partitioning of the liquid phase into mobile and immobile parts, but also considers the uneven distribution of adsorption sites between the intra- and inter-ag-

TABLE I

Summary of the dimensionless transport models discussed in this study

Model type	Mobile liquid phase transport equation	Stagnant phase transport equation	Average intra-aggregate concentration	Equation numbers
Linear equilibrium (LE)	$R\frac{\partial c}{\partial T} = \frac{1}{P}\frac{\partial^2 c}{\partial Z^2} - \frac{\partial c}{\partial Z}$	—	—	A1
First-order (FO)	$\beta R\frac{\partial c_m}{\partial T} + (1-\beta)R\frac{\partial c_{im}}{\partial T} = \frac{1}{P_m}\frac{\partial^2 c_m}{\partial Z^2} - \frac{\partial c_m}{\partial Z}$	—	$(1-\beta)R\frac{\partial c_{im}}{\partial T} = \omega(c_m - c_{im})$	A2, A3
Spherical aggregates (SD)	Same as FO	$\frac{\partial c_a}{\partial T} = \frac{\gamma_s}{\zeta^2}\frac{\partial}{\partial \zeta}(\zeta^2\frac{\partial c_a}{\partial \zeta})$	$c_{im} = 3\int_0^1 \zeta^2 c_a d\zeta$	A4, A5
Rectangular aggregates (RD)	Same as FO	$\frac{\partial c_a}{\partial T} = \gamma_1\frac{\partial^2 c_a}{\partial X^2}$	$c_{im} = \int_0^1 c_a dX$	A6, A7
Solid cylindrical aggregates (SCD)	Same as FO	$\frac{\partial c_a}{\partial T} = \frac{\gamma_c}{\zeta}\frac{\partial}{\partial \zeta}(\zeta\frac{\partial c_a}{\partial \zeta})$	$c_{im} = 2\int_0^1 \zeta c_a d\zeta$	A8, A9
Hollow cylindrical macropores (HCD)	Same as FO	$\frac{\partial c_a}{\partial T} = \frac{\gamma_p}{\zeta}\frac{\partial}{\partial \zeta}(\zeta\frac{\partial c_a}{\partial \zeta})$	$c_{im} = \frac{2}{\zeta_0^2 - 1}\int_1^{\zeta_0} \zeta c_a d\zeta$	A10, A11

TABLE II

Dimensionless parameters used for the transport models listed in Table I

Model	Type	Dimensionless parameters				
LE	Linear equilibrium	$T = \frac{vt}{L}$ $Z = \frac{z}{L}$	—	$P = \frac{vL}{D}$	—	—
FO	First-order	$T = \frac{qt}{\theta L}$ $Z = \frac{z}{L}$	—	$P_{\mathrm{m}} = \frac{v_{\mathrm{m}} L}{D_{\mathrm{m}}}$	$\beta = \frac{\theta_{\mathrm{m}} R_{\mathrm{m}}}{\theta R}$	$\omega = \frac{\alpha L}{q}$
SD	Spherical aggregates	Same as FO	$\zeta = \frac{r}{a_{\mathrm{s}}}$	Same as FO		$\gamma_{\mathrm{s}} = \frac{D_{\mathrm{a}} \theta L}{a_{\mathrm{s}}^2 q R_{\mathrm{im}}}$
RD	Rectangular aggregates	Same as FO	$X = \frac{x}{a_{\mathrm{l}}}$	Same as FO		$\gamma_{\mathrm{l}} = \frac{D_{\mathrm{a}} \theta L}{a_{\mathrm{l}}^2 q R_{\mathrm{im}}}$
SCD	Solid cylindrical aggregates	Same as FO	$\zeta = \frac{r}{a_{\mathrm{c}}}$	Same as FO		$\gamma_{\mathrm{c}} = \frac{D_{\mathrm{a}} \theta L}{a_{\mathrm{c}}^2 q R_{\mathrm{im}}}$
HCD	Hollow cylindrical macropores	Same as FO	$\zeta = \frac{r}{a_{\mathrm{p}}}; \zeta_0 = \frac{b}{a_{\mathrm{p}}}$	Same as FO		$\gamma_{\mathrm{p}} = \frac{D_{\mathrm{a}} \theta L}{a_{\mathrm{p}}^2 q R_{\mathrm{im}}}$

gregate regions:

$$\beta = \frac{\theta_m R_m}{\theta_m R_m + \theta_{im} R_{im}} = \frac{\theta_m R_m}{\theta R} \tag{4}$$

where as before R is the total retardation factor of the soil system. More detailed discussions of the dimensionless models and their parameters are given elsewhere (van Genuchten et al., 1984; van Genuchten, 1985). Table I also contains the dimensionless form of eq. 1, hereafter referred to as the linear equilibrium (LE) model. All concentrations c in this study are made dimensionless by using transformations of the form:

$$c = \frac{C - C_i}{C_0 - C_i} \tag{5}$$

where C = dimensioned concentration, C_i = initial concentration, and C_0 = applied input concentration at $z = 0$.

The following initial and boundary conditions are applied to all models (for the LE model, c_m and P_m must be replaced by c and P, respectively):

$$c_m(Z,0) = 0 \qquad c_{im}(Z,0) = 0 \tag{6a, b}$$

$$c_m(0,T) - \frac{1}{P_m}\frac{\partial c_m}{\partial Z}(0,T) = 1 \qquad \frac{\partial c_m}{\partial Z}(\infty, T) = 0 \tag{6c, d}$$

Using a variety of tracers (tritiated water, chloride, pesticides, heavy metals), the FO model has been quite successful in describing many asymmetrical laboratory-scale displacement processes (Coats and Smith, 1964; Gaudet et al., 1979; Nkedi-Kizza et al., 1983; among others). However, its use as a predictive tool for field-scale studies has been limited. The main reason for its limited use is the obscure dependency of the mass transfer coefficient α on the diffusion properties of aggregates (notably aggregate geometry and the diffusion coefficient). In general, values for α, and to some extent the immobile water content θ_{im}, must be fitted to observed data before the model can be used. This is especially true for soils that contain small, poorly defined aggregates, and ironically also for seemingly homogeneous and repacked soils. Because of the diffuse spatial location and configuration of immobile water pockets and associated sorption sites, α and θ_{im} for such soils are difficult to quantify by other than curve-fitting techniques (van Genuchten, 1981; Parker and van Genuchten, 1984).

TRANSPORT IN GEOMETRICALLY WELL-DEFINED SYSTEMS

Geometry is somewhat less of a problem when simulating transport in soils made up of uniformly-sized and -shaped aggregates. Transport models for such systems are briefly discussed below. Again, the dimensionless forms of the models and their main parameters are summarized in Tables I and II. All models in Table I have been solved analytically; the solutions are given elsewhere (van Genuchten, 1985; Parker and Valocchi, 1986). Calculated concentrations in this study are understood to represent flux-averaged values.

Spherical aggregates (SD)

Transport equation 2 for the mobile liquid phase holds for all tworegion models irrespective of aggregate geometry, provided that c_{im} is taken to be the average concentration of the immobile liquid phase. For a soil made up of uniformly-sized spherical aggregates, c_{im} is simply the average concentration of a sphere:

$$c_{\mathrm{im}}(z,t) = \frac{3}{a_{\mathrm{s}}^3} \int_0^{a_{\mathrm{s}}} r^2 c_{\mathrm{a}}(z,r,t)\,\mathrm{d}r \tag{7}$$

where r = radial coordinate, a_{s} = radius of sphere, and c_{a} = local fluid concentration of spherical aggregate.

Solute transfer in the aggregate is governed by the spherical diffusion equation:

$$R_{\mathrm{im}} \frac{\partial c_{\mathrm{a}}}{\partial t} = \frac{D_{\mathrm{a}}}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c_{\mathrm{a}}}{\partial r}\right) \qquad (0 \leqslant r \leqslant a_{\mathrm{s}}) \tag{8}$$

where D_{a} = effective diffusion coefficient of the aggregate.

The transport equations are augmented with auxiliary conditions requiring concentration continuity at the macropore walls (eq. 9a) and a zero concentration gradient at $r = 0$ (eq. 9b):

$$c_{\mathrm{m}}(z,t) = c_{\mathrm{a}}(z,a_{\mathrm{s}},t) \qquad \frac{\partial c_{\mathrm{a}}}{\partial r}(z,0,t) = 0 \tag{9a, b}$$

Rectangular aggregates (RD)

The average immobile liquid phase concentration c_{im} for line-sheet type aggregates separated by parallel rectangular voids is:

$$c_{\mathrm{im}}(z,t) = \frac{1}{a_{\mathrm{l}}} \int_0^{a_{\mathrm{l}}} c_{\mathrm{a}}(z,x,t)\,\mathrm{d}x \tag{10}$$

where a_{l} = half the width of the rectangular aggregate, and x = coordinate perpendicular to the aggregate wall.

Solute transfer inside the aggregates is governed by the linear diffusion equation:

$$R_{\mathrm{im}} \frac{\partial c_{\mathrm{a}}}{\partial t} = D_{\mathrm{a}} \frac{\partial^2 c_{\mathrm{a}}}{\partial x^2} \qquad (0 \leqslant x \leqslant a_{\mathrm{l}}) \tag{11}$$

Boundary conditions for the aggregate are in this case:

$$c_{\mathrm{m}}(z,t) = c_{\mathrm{a}}(z,a_{\mathrm{l}},t) \qquad \frac{\partial c_{\mathrm{a}}}{\partial x}(z,0,t) = 0 \tag{12a, b}$$

Solid cylindrical aggregates (SCD)

The average immobile phase concentration at any depth z is:

$$c_{\mathrm{im}}(z,r,t) = \frac{2}{a_{\mathrm{c}}^2} \int_0^{a_{\mathrm{c}}} r\, c_{\mathrm{a}}(z,r,t)\, \mathrm{d}r \tag{13}$$

where r = radial coordinate, and a_{c} = radius of the solid cylinder.

The local concentration c_{a} in the aggregates is determined by the cylindrical diffusion equation:

$$R_{\mathrm{im}} \frac{\partial c_{\mathrm{a}}}{\partial t} = \frac{D_{\mathrm{a}}}{r} \frac{\partial}{\partial r}\left(r \frac{\partial c_{\mathrm{a}}}{\partial r}\right) \qquad (0 \leqslant r \leqslant a_{\mathrm{c}}) \tag{14}$$

The internal boundary conditions are:

$$c_{\mathrm{m}}(z,t) = c_{\mathrm{a}}(z,a_{\mathrm{c}},t) \qquad \frac{\partial c_{\mathrm{a}}}{\partial r}(z,0,t) = 0 \tag{15a, b}$$

Hollow cylindrical macropores (HCD)

The average micropore concentration for this model is:

$$c_{\mathrm{im}}(z,t) = \frac{2}{b^2 - a_{\mathrm{p}}^2} \int_{a_{\mathrm{p}}}^{b} r\, c_{\mathrm{a}}(z,r,t)\, \mathrm{d}r \tag{16}$$

where a_{p} is the radius of the macropore, b is the radius of the finite cylinder of soil surrounding the macropore, while r again represents the radial coordinate. Solute transfer in the soil matrix is described by:

$$R_{\mathrm{im}} \frac{\partial c_{\mathrm{a}}}{\partial t} = \frac{D_{\mathrm{a}}'}{r} \frac{\partial}{\partial r}\left(r \frac{\partial c_{\mathrm{a}}}{\partial r}\right) \qquad (a_{\mathrm{p}} \leqslant r \leqslant b) \tag{17}$$

with the boundary conditions:

$$c_{\mathrm{m}}(z,t) = c_{\mathrm{a}}(z,a_{\mathrm{p}},t) = 0 \qquad \frac{\partial c_{\mathrm{a}}}{\partial r}(z,b,t) = 0 \tag{18a, b}$$

EXTENSION TO OTHER GEOMETRIES

Analytical solutions are currently only available for the five two-region models listed in Table I. Exact solutions have not been derived for other systems, notably for finite prismatic or columnar aggregates. To make the limited set of solutions applicable to other aggregate geometries, an approach using shape factors was formulated by van Genuchten (1985). The main objective of the procedure is to convert a soil made up of aggregates of any arbitrary geometry into a reference soil for which an analytical two-region type transport model is available. An obvious candidate for such a reference soil is a soil made up of uniformly-sized spherical aggregates, although in reality any geometry can be used for which an analytical two-region model exists (Table I). The conversion method uses a geometry-dependent shape factor f that converts an aggregate of arbitrary geometry into an "equivalent" sphere with the same average diffusion characteristics as the original aggregate. The conversion procedure is briefly discussed below.

Inspection of Table I shows that the mobile phase transport eq. A2 applies to all two-region models irrespective of aggregate geometry. The five two-region models differ only with respect to the rate by which material diffuses from the macropore fluid into the soil matrix (and vice versa). This is reflected by different equations for the average immobile concentration c_{im} as a function of time. Thus, if for a given model we can closely approximate c_{im} with some simplified expression, then the approximate result should be close to the correct prediction.

As an example, let us compare the c_{im} expressions for the spherical (SD) and rectangular (RD) two-region transport models. Applying Laplace transforms to eq. A4 of Table I, using boundary conditions 9a, b and a zero initial condition for c_a leads to

$$\bar{c}_a(Z,\zeta,s) = \frac{\sinh(p\zeta)}{\zeta \sinh(p)}\, \bar{c}_m(Z,s) \qquad (p = \sqrt{s/\gamma_s}) \tag{19}$$

where $\bar{c}$ = Laplace transform of c with respecto to T, and s = Laplace transform parameter.

Substituting eq. 19 into the Laplace transform of eq. A5 in Table I and integrating gives:

$$\bar{c}_{im} = \left[\frac{3}{p}\coth(p) - \frac{3}{p^2}\right] \bar{c}_m \tag{20}$$

Substituting the first three terms of the series:

$$\coth(p) = \frac{1}{p} + \frac{p}{3} - \frac{p^3}{45} + \frac{2p^5}{945} + \ldots \tag{21}$$

into eq. 20 leads to the following approximation for $\bar{c}_{\text{im}}$ (note that $p^2 = s/\gamma_s$):

$$\bar{c}_{\text{im}} = \left(1 - \frac{s}{15\gamma_s}\right)\bar{c}_{\text{m}} \tag{22}$$

A similar equation can also be derived for the RD model:

$$\bar{c}_{\text{im}} = \sqrt{p}\,\tanh(\sqrt{p})\,\bar{c}_{\text{m}} \qquad (p = \sqrt{s/\gamma_l}) \tag{23}$$

or with the approximation $\tanh(p) = p - p^3/3 + \ldots$

$$\bar{c}_{\text{im}} = \left(1 - \frac{s}{3\gamma_l}\right)\bar{c}_{\text{m}} \tag{24}$$

Equating eqs. 22 and 24 gives the following relation between the dimensionless parameters γ_s and γ_l:

$$\gamma_s = \gamma_l/5 \tag{25}$$

or with the definitions of γ_s and γ_l (Table II):

$$a_s = \left(\frac{\gamma_l}{\gamma_s}\right)^{1/2} a_l = \sqrt{5}\,a_l = 2.24\,a_l \tag{26}$$

The constant 2.24 is called the shape factor $f_{l,s}$ for conversion from a line-sheet type aggregate (subscript l) into a spherical aggregate (subscript s) with similar diffusion properties. In other words, the time-dependent average concentration of a rectangular aggregate having a width of 1 cm should be very similar to the average concentration of a sphere having a diameter of 2.24 cm, as long as both aggregates are subjected to the same initial and boundary conditions. Note that in this approach the rectangular and spherical aggregates do not necessarily have the same volumes. Aggregate volumes have already been taken into account implicitly through the proper definition of the mobile and immobile water contents (θ_{m} and θ_{im}) in the transport equations.

Because of several approximations in the derivation, eq. 26 will not be exact. Moreover, the expressions for c_{im} are nonlinear in s, and hence in t, which should make the shape factor $f_{l,s}$ time-dependent. A slightly different value for the shape factor was derived earlier (van Genuchten, 1985) by directly matching average concentrations of various aggregates in nonflowing system. In that paper we obtained a value of 2.54 for $f_{l,s}$, which leads to:

$$\gamma_s = \gamma_l/6.4. \tag{27}$$

Fig. 2a compares calculated breakthrough curves, $c_e(T) = c_{\text{m}}(1,T)$, for transport through a soil containing rectangular aggregates using both the

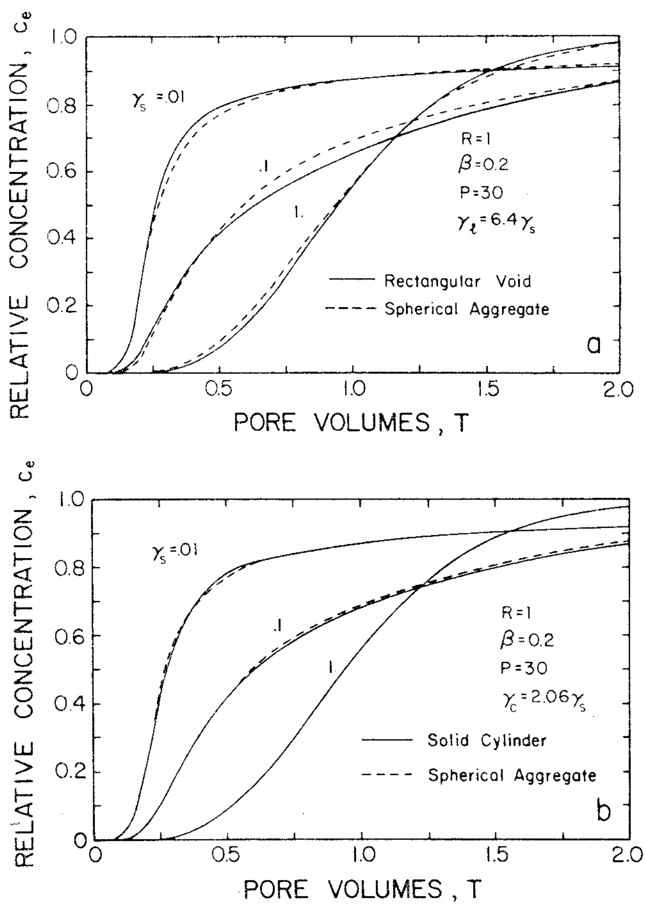

Fig. 2. Breakthrough curves calculated with the equivalent spherical (SD) model and the exact curves for (a) rectangular aggregates (RD) and (b) solid cylindrical aggregates (SCD) (after van Genuchten, 1985).

exact RD model and the approximate spherical SD model. While not perfect, the SD model certainly gives a reasonable approximation of the RD model. The same procedure using Laplace transforms can also be used for the solid cylindrical diffusion (SCD) transport model. The Laplace transform of c_{im} in this case is:

$$\bar{c}_{im} = \frac{2\, I_1\,(p)}{p\, I_0\,(p)} \qquad (p = \sqrt{s/\gamma_c}) \tag{28}$$

Using expansions for the Bessel functions I_0 and I_1 for small values of p, eq. 28 can be approximated by:

$$\bar{c}_{im} = (1 - \frac{s}{8\gamma_c})\, \bar{c}_m \tag{29}$$

Equating eqs. 22 and 29 now gives:

$$\gamma_s = \frac{8}{15}\gamma_c \qquad (30)$$

which leads to a shape factor $f_{c,s}$ of 1.37. This is again close to the value of 1.44 obtained by directly matching average concentrations of spherical and solid cylindrical aggregates (van Genuchten, 1985). The latter value of 1.44 for the shape factor gives $\gamma_s = \gamma_c/2.06$, which results in the approximation as shown in Fig. 2b. Clearly, the approximation using equivalent spheres works better for solid cylindrical than for rectangular aggregates. This should be no surprise since the surface-area/volume ratio of a sphere is much closer to the surface/volume ratio of a solid cylinder (of unit height) than that of a rectangular slab.

Success of the transformation into equivalent spherical aggregates can be judged from Fig. 3, which shows plots of the relative shape factor (f/f_{50}) as a function of the average aggregate concentration. The relative shape factor is defined as the value of the shape factor at any concentration relative to its value at $\langle c_a \rangle \equiv c_{im} = 0.5$. The closer the curves in Fig. 3 remain to one, the better the approximation into equivalent spheres. From Figs. 2 and 3 we may conclude that most finite rectangular and cylindrical

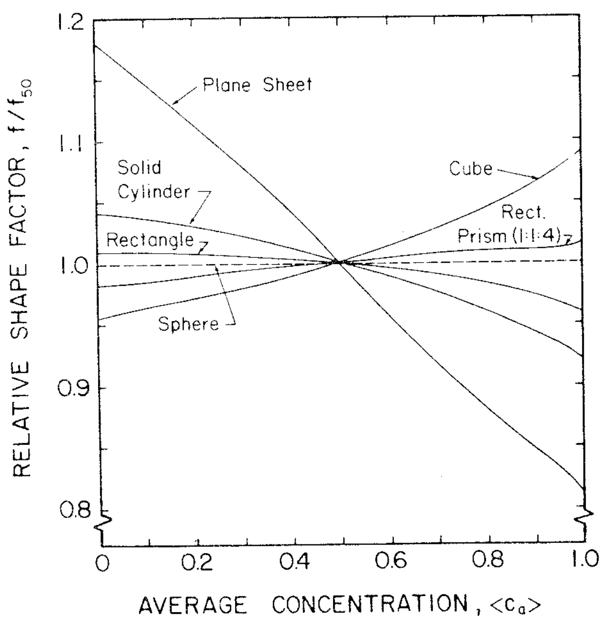

Fig. 3. Effect of the average concentration on the relative shape factor for conversion of several aggregate geometries into equivalent spherical aggregates (after van Genuchten, 1985).

aggregates can be approximated accurately with spherical equivalents, while the conversion from plane sheets to spheres will be somewhat less accurate, but perhaps still acceptable for most applications. Not plotted in Fig. 3 is the relative shape factor for the conversion of hollow cylindrical macropore systems into equivalent spherical systems. The relative shape factor for this conversion is considerably more concentration-dependent than those shown in Fig. 3. Thus the HCD-model (Table II) cannot be approximated accurately with the SD model.

We note that Barker (1985) recently proposed a method using "block-geometry functions" that somewhat resembles the above approach based on shape factors. The block-geometry functions are essentially identical to the Laplace transforms of the average immobile concentration, $\bar{c}_{\mathrm{im}}$, as listed in this study. Barker combined the shape-dependent functions with the Laplace transform for the mobile concentration, $\bar{c}_{\mathrm{m}}$, and then used numerical Laplace inversion techniques to obtain solutions for c_{m}. By introducing empirical block-geometry functions for less well-defined systems, his method could prove to be especially useful for modeling transport in soils containing aggregate mixtures of different shapes and sizes. An alternative way of dealing with aggregate mixtures was recently explored by Neretnieks and Rasmuson (1984).

COMPARISONS WITH THE FIRST-ORDER (FO) MODEL

The scaling method can also be used to obtain approximate equations for the mass transfer coefficients α and ω that appear in the first-order rate (FO) model. This is done by again comparing the Laplace transforms of c_{im}. The transform of eq. A3 (Table I) for the FO model gives:

$$(1-\beta)Rs\,\bar{c}_{\mathrm{im}} = \omega(\bar{c}_{\mathrm{m}} - \bar{c}_{\mathrm{im}}) \tag{31}$$

Solving for $\bar{c}_{\mathrm{im}}$ leads to:

$$\bar{c}_{\mathrm{im}} = \frac{\omega}{\omega + (1-\beta)Rs}\,\bar{c}_{\mathrm{m}} \tag{32}$$

or to a first approximation:

$$\bar{c}_{\mathrm{im}} = \left[1 - \frac{(1-\beta)Rs}{\omega}\right]\,\bar{c}_{\mathrm{m}} \tag{33}$$

Comparison with eq. 22 for the SD-model gives:

$$\omega = 15\,(1-\beta)R\gamma_{\mathrm{s}} \tag{34}$$

which compares well with the relation:

$$\omega = 22.7\,(1-\beta)R\gamma_{\mathrm{s}} \tag{35}$$

that was derived by directly matching average concentrations at $c_{im} = 0.5$ (van Genuchten, 1985). Eq. 34 was also obtained by Parker and Valocchi (1986) by comparing second moments of the two transport models.

Fig. 4a shows that the first-order model with eq. 35 does not provide a good approximation for transport through a soil with spherical aggregates. However, the same FO-model gives an excellent approximation for a hollow cylindrical macropore (HCD) system. In this case, the Laplace transform of c_{im} is given by (van Genuchten et al., 1984):

$$\bar{c}_{im} = \frac{I_1(p\zeta_0)K_1(p) - I_1(p)K_1(p\zeta_0)}{I_0(p)K_1(p\zeta_0) + I_1(p\zeta_0)K_0(p)} \; \frac{2}{p(\zeta_0 - 1)^2} \; \bar{c}_m \qquad (p = \sqrt{s/\gamma_p}) \tag{36}$$

With a considerable amount of algebra, eq. 36 for $\zeta_0 >> 1$ can be shown to reduce to:

$$\bar{c}_{im} = \left\{ 1 - \frac{\zeta_0^2}{2\gamma_p} \, [\ln(\zeta_0) - 1] \, s \right\} \bar{c}_m \tag{37}$$

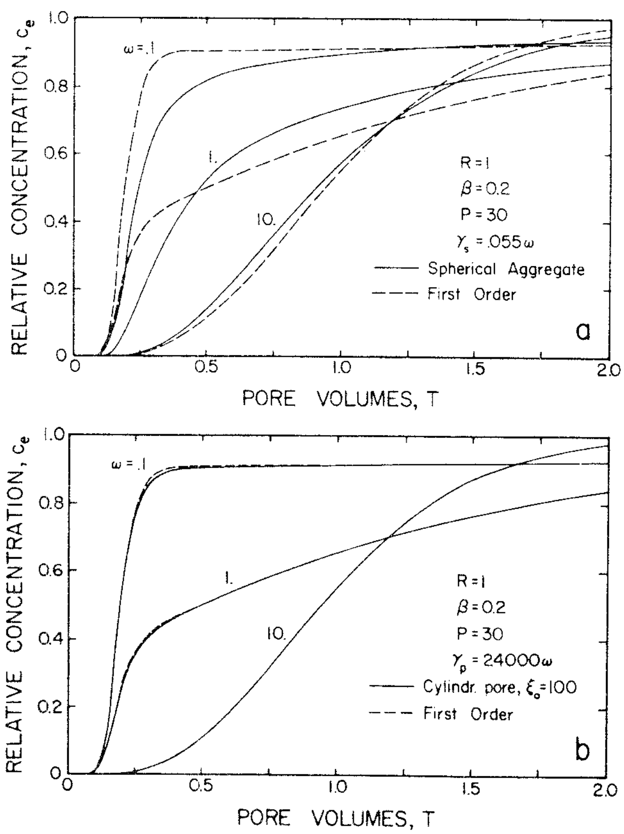

Fig. 4. Exact and first-order approximate solutions for transport through soils containing (a) spherical aggregates and (b) hollow cylindrical macropores (after van Genuchten, 1985).

Equating eqs. 33 and 37 leads to:

$$\omega = \frac{2(1-\beta)R\gamma_p}{\zeta_0^2\,[\ln(\zeta_0)-1]} \tag{38}$$

For $\zeta_0 = 100, \beta = 0.2$ and $R = R_{im} = 1$, eq. 38 predicts:

$$\omega = \gamma_p/22530 \tag{39}$$

which is again very close to the relation $\omega = \gamma_p/24000$ obtained by directly matching average concentrations in a non-flowing system (van Genuchten, 1985). The latter relation was used for the comparison of the HCD and FO models in Fig. 4b.

From Figs. 2, 3 and 4, as well as from numerous other calculations (van Genuchten, 1985), we conclude that the first-order model accurately predicts transport through soils containing large continuous cylindrical macropores, whereas the spherical model is more accurate for soils that are structured in other ways.

EQUIVALENT DISPERSION COEFFICIENTS FOR THE LINEAR EQUILIBRIUM MODEL

The Laplace transorms for c_{im} given earlier can be used also to derive expressions for an "effective" or equivalent dispersion coefficient D_e for use in the linear equilibrium (LE) model. The main purpose of the exercise is to find a correction for the dispersion coefficient so that D_e includes to a first approximation the effects of intra-aggregate diffusion. The procedure below is very similar to the one used by Raats (1981).

As a first example, consider again the spherical diffusion (SD) model. Taking the Laplace transform of eq. A2 yields:

$$\beta Rs\,\bar{c}_m + (1-\beta)Rs\,\bar{c}_{im} = \frac{1}{P_m}\frac{\partial^2 \bar{c}_m}{\partial Z^2} - \frac{\partial \bar{c}_m}{\partial Z} \tag{40}$$

Eq. 22 gives a first-order approximation of $\bar{c}_{im}$ in terms of the mobile concentration $\bar{c}_m$. Substituting that relation into eq. 40 lead to:

$$Rs\,\bar{c}_m = \frac{1}{P_m}\frac{\partial^2 \bar{c}_m}{\partial Z^2} - \frac{\partial \bar{c}_m}{\partial Z} + \frac{(1-\beta)Rs^2}{15\gamma_s}\,\bar{c}_m \tag{41}$$

or after inversion:

$$R\frac{\partial c_m}{\partial T} = \frac{1}{P_m}\frac{\partial^2 \bar{c}_m}{\partial Z^2} - \frac{\partial c_m}{\partial Z} - \frac{(1-\beta)R}{15\gamma_s}\frac{\partial^2 c_m}{\partial T^2} \tag{42}$$

Comparison with eq. A2 of Table I shows that the factor β has been removed from the time derivative of c_m on the left hand side, which suggests that c_m now represents the average concentration c of the mobile *and* immobile liquid phases. The second time derivative (last term of eq.

42) can be transformed into a second spatial derivative by noting that from eq. 42 to a first approximation:

$$\frac{\partial c}{\partial T} = -\frac{1}{R}\frac{\partial c}{\partial Z} \tag{43}$$

or by repeating the same change of differentiation:

$$\frac{\partial^2 c}{\partial T^2} = \frac{1}{R^2}\frac{\partial^2 c}{\partial Z^2} \tag{44}$$

Substituting eq. 44 into eq. 42 and dropping the subscripts m gives finally:

$$R\frac{\partial c}{\partial T} = \frac{1}{P_e}\frac{\partial^2 c}{\partial Z^2} - \frac{\partial c}{\partial Z} + E \tag{45}$$

where:

$$\frac{1}{P_e} = \frac{1}{P_m} + \frac{1-\beta}{15\gamma_s R} \tag{46}$$

and where E is the error introduced when the spherical diffusion model is approximated by eq. 45. Note that eq. 45 is identical to the linear equilibrium model, except that the equation contains a modified Peclet number P_e that includes the effects of intra-aggregate diffusion. Using the dimensionless parameters of Table II, eq. 46 leads to the following equation for the effective dispersion coefficient:

$$D_e = D_m\phi_m + \frac{(1-\phi_m)\,a_s^2 v^2 R^2{}_{im}}{15 D_a R^2} \qquad (\phi_m = \theta_m/\theta), \tag{47}$$

which shows that the dispersion coefficient of an aggregated system increases with increasing aggregate size and pore-water velocity and decreasing soil matrix diffusion coefficient D_a. By comparing the second moments of the linear and spherical diffusion transport models, Parker and Valocchi (1986) were also able to derive eq. 47. Similar equations were also obtained by Passioura (1971) for a non-adsorbing system ($R = 1$), and more recently by Bolt (1979). By using eq. 47 in the LE model, Parker and Vallocchi (1986) obtained a surprisingly accurate approximation of the spherical diffusion model for several sets of parameters. While we believe that the accuracy of eq. 47 remains to be demonstrated for a wide range of parameters (especially for intermediate values of β), the results of Parker and Valocchi (1985) clearly indicate that the linear equilibrium model can provide at times an excellent approximation for the spherical diffusion model. The error E of eq. 45 can be approximated by carrying in the above derivation an addition term $(2p^2/945)$ of the coth series expansion given by eq. 21. Without giving details of the derivation, we obtained the following result:

$$E = \frac{2(1-\beta)}{15\gamma_s}\left(\frac{1}{P_m} + \frac{2-7\beta}{105\gamma_s R}\right)\frac{\partial^3 c}{\partial z^3} \tag{48}$$

which closely resembles the error derived by Parker and Valocchi (1985) using moment analyses.

The same procedure as above can be applied also to the other two-region models. For completeness, and without repeating the individual steps, the final results are given below. The following equation was obtained for the rectangular (RD) model:

$$D_e = D_m\phi_m + \frac{(1-\phi_m)\, a_l^2 v^2 R_{im}^2}{3D_a R^2} \tag{49}$$

Similar equations were also derived by Bolt (1979) and by Raats (1981), the latter author using the same Laplace transform methodology. For the solid cylindrical diffusion (SCD) model we obtained:

$$D_e = D_m\phi_m + \frac{(1-\phi_m)\, a_c^2 v^2 R^2{}_{im}}{8D_a R^2} \tag{50}$$

which is again consistent with Bolt's analysis (Bolt, 1979, p. 307), and for the hollow cylindrical macropore (HCD) system:

$$D_e = D_m\phi_m + \frac{[2\ln(b/a_p)-1]\,(1-\phi_m)\, v^2 b^2 R_{im}^2}{4D_a R^2} \tag{51}$$

Finally, a similar equation can also be derived for the first-order model. The equivalent Peclet number and dispersion coefficients for this case are:

$$\frac{1}{P_e} = \frac{1}{P_m} + \frac{(1-\beta)^2}{\omega} \tag{52}$$

and:

$$D_e = D_m\phi_m + \frac{(1-\phi_m)^2 v^2 R_{im}^2\,\theta}{\alpha R^2} \tag{53}$$

SUMMARY AND CONCLUSIONS

Several two-region models for simulating salt movement in aggregated soils are discussed. A common feature of these models is the assumption that solutes are being transported through well-defined pores and cracks of known geometry, while diffusion-type equations are used to describe solute transfer inside the micropores of the soil matrix. Analytical two-region models are currently available for spherical, cylindrical and line-sheet type aggregates. Another solution exists for transport through large cylindrical macropores. A scaling method is discussed that extends the analytical two-region modeling approach to other aggregate geometries. The method uses a geometry-dependent shape factor to replace a given aggregate by an "equivalent" sphere with approximately the same average diffusion properties as the original aggregate.

The transformations were found to work well for most structured systems, except for soils containing hollow cylindrical macropores. The same scaling method is also used to relate the mass transfer coefficient in a first-order rate model to measurable soil-physical parameters. The latter model gives an excellent approximation for transport through hollow cylindrical macropores, but is considerably less accurate for spherically aggregated and related systems. Finally, Laplace transform techniques are used to derive several equations that lump the effects of intra-aggregate diffusion on transport into an effective dispersion coefficient for use in the classical two-parameter transport equation.

ACKNOWLEDGEMENTS

The authors greatly benefitted from discussions with J.C. Parker and A.J. Valocchi. We especially appreciated receiving an advanced copy of their paper (Parker and Valocchi, 1986) presented at this conference. While certain features of the Laplace transform procedure used in our paper were first discussed by Raats (1981), the applications in the Parker and Valocchi paper provided additional incentives for our work.

REFERENCES

Barker, J.A., 1985. Block-geometry functions characterizing transport in densely fissured media. J. Hydrol., 77: 263—279.

Bolt, G.H., 1979. Movement of solutes in soil: principles of adsorption/exchange chromatography. In: G.H. Bolt (Editor), Soil Chemistry, B. Physico-Chemical Models. Developments in Soil Science 5B, Elsevier, Amsterdam, pp. 295—348.

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

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

Gaudet, J.P., Jegat, H., Vachaud, G. and Wierenga, P.J., 1977. Solute transfer, with diffusion between mobile and stagnant water, through unsaturated sand. Soil Sci. Soc. Am. J., 41: 665—671.

Neretnieks, I. and Rasmuson, A., 1984. An approach to modelling radionuclide migration in a medium with strongly varying velocity and block sizes along the flow path. Water Resour. Res., 20: 1823—1836.

Nkedi-Kizza, P., Biggar, J.W., van Genuchten, M.Th., Wierenga, P.J., Selim, H.M., Davidson, J.M. and Nielsen, D.R., 1983. Modeling tritium and chloride-36 transport through an aggregated oxisol. Water Resour. Res., 19: 691—700.

Parker, J.C. and Valocchi, A.J., 1986. Constraints on the validity of equilibrium and first-order kinetic transport models in structured soils. Water Resour. Res. In press.

Parker, J.C. and van Genuchten, M.Th., 1984. Determining transport parameters from laboratory and field tracer experiments. Virginia Agricultural Exp. Station, Bull., 84-3, 96 pp.

Passioura, J.B., 1971. Hydrodynamic dispersion in aggregated media. Soil Sci., 111: 339—344.

Raats, P.A.C., 1981. Transport in structured porous media. Proc. Euromech. 143, September 2—4, Delft, pp. 221—226.

Rasmuson, A. and Neretnieks, I., 1980. Exact solution for diffusion in particles and longitudinal dispersion in packed beds. Am. Inst. Chem. Eng. J., 26: 686—690.

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

Thomas, G.W. and Phillips, R.E., 1979. Consequences for water movement in macropores. J. Environ. Qual., 8: 149—152.

Valocchi, A.J., 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. Water Resour. Res., 21: 808—820.

van Genuchten, M.Th., 1981. Non-equilibrium transport parameters from miscible displacement experiments. Res. Rep. 119, U.S. Salinity Laboratory, Riverside, Calif., 88 pp.

van Genuchten, M.Th., 1985. A general approach for modeling solute transport in structured soils. Proc. 17th Int. Congress, IAH, Hydrogeology of Rocks of Low Permeability, Jan. 7—12, 1973, Tucson, AZ. Mem. Int. Assoc. Hydrogeol., 17(2): 513—526.

van Genuchten, M.Th. and Wierenga, P.J., 1976. Mass transfer studies in sorbing porous media, I. Analytical solutions. Soil Sci. Soc. Am. J., 40: 473—480.

van Genuchten, M.Th., Tang, D.H. and Guennelon, R., 1984. Some exact and approximate solutions for solute transport through large cylindrical macropores. Water Resour. Res., 20: 335—346.

White, R.E., 1985. The influence of macropores on the transport of dissolved and suspended matter through soil. Adv. Soil Sci., 3: 95—120.

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