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Modeling the Nonequilibrium Transport of Linearly Interacting Solutes in Porous Media: A Review

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The transport of linearly interacting solutes in porous media is investigated with the help of residence time distributions, transfer functions, methods of system dynamics, and time-moment analyses. The classical one-dimensional convection-dispersion equation is extended to two-region (mobile-immobile water) transport by including diffusional mass transfer limitations characteristic of aggregated soils. The two-region model is further revised by incorporating the effects of multiple retention sites (in parallel or in series), multiple porosity levels, and arbitrary but steady flow fields. It is shown that different physical situations can be represented by a relatively small number of transfer functions containing only two types of parameters: distribution coefficients to account for equilibrium properties and characteristic times reflecting kinetic processes. Relevant kinetic processes include convective transport, hydrodynamic dispersion, adsorption-desorption, and physical or chemical mass transfer limitations. In most situations, theoretical breakthrough curves are found to be relatively insensitive to the mathematical structure of the transfer function, irrespective of the physical interpretation of the distribution coefficients and the characteristic times in the model. This means that alternative physical and chemical interpretations of model parameters can lead to nearly identical breakthrough curves. Certain transfer time distributions can lead to quite unusual shapes in the breakthrough curves; these curves strongly depend on the characteristic times and a few operational variables. Results of this study show that the transfer time distribution is an extremely useful tool for explaining some unexpected experimental results in the solute transport literature.

1. INTRODUCTION

Solute transport in soil and groundwater systems is affected by a large number of complicated and often interactive physical, chemical, and microbiological processes. During the past several decades, numerous models have been developed to evaluate the transport of linearly interacting solutes in porous media. Most models were initially based on the classical one-dimensional convection-dispersion equation, as exemplified by the studies of *Lapidus and Amundson* [1952] and *Nielsen and Biggar* [1962]. Starting with the historical papers of *Coats and Smith* [1964] and *Villermaux and van Swaaij* [1969], authors later derived one-dimensional and multidimensional models for increasingly complicated processes and soil properties. This was done by extending the models to include different types of sorption sites, a variety of expressions characterizing physical and chemical nonequilibrium, and alternative geometries of immobile (stagnant) liquid phases in the medium [*Gaudet et al.*, 1977; *de Smedt and Wierenga*, 1979; *van Genuchten and Cleary*, 1979; *Schultz and Reardon*, 1983; *Valocchi*, 1985; *Brusseau et al.*, 1989]. Most of these studies focused on the formulation of appropriate mass balance (partial differential) equations governing solute transport, the derivation of appropriate analytical or numerical solutions of those equations, and the ability or inability of the transport equations to match observed solute distributions versus time or distance. More recently, moment analysis techniques also appeared in the soil and groundwater literature [*Valocchi*, 1985, 1989, 1990; *Sposito et al.*, 1986; *Goltz and Roberts*, 1987].

At the same time, the study of reactors in chemical engineering led to the development of alternative methods for simulating the transport of reactive solutes during nonideal flow, particularly dispersed plug flow [*Himmelblau and Bischoff*, 1968; *Levenspiel*, 1972; *Wen and Fan*, 1975; *Villermaux*, 1982; *Nauman and Buffham*, 1983]. Many researchers applied principles of linear system dynamics and ideal reactors to more efficiently model increasingly complex chemical systems. At present, one of the most powerful tools in chemical reaction engineering is the concept of residence time distribution which permits one to describe the main properties of a transport system with only a few key parameters, especially when the solute interacts linearly with the porous medium. This approach was first introduced in hydrology by Jury and coworkers [*Jury*, 1982; *Jury and Sposito*, 1986; *White et al.*, 1986; *Sposito et al.*, 1986; *Jury and Roth*, 1990].

Although the prediction of water flow in a soil requires a detailed physical or mechanical approach, the transport of linearly interacting solutes in a given flow regime requires only knowledge of the residence time distribution. The purpose of this paper is to critically review various predictive approaches based on the residence time distribution concept. After recalling some basic definitions from linear system dynamics we shall first apply the residence time distribution concept to classical description of one-dimensional convective-dispersive solute transport with and without mass transfer limitations. Next, a relatively simple, yet very general method will be discussed to gradually build

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increasingly complex solute transport models with comparatively little mathematical effort. Special emphasis is placed on model structure and parameter interpretation. We shall also show that many nonequilibrium solute transport models in the literature are essentially identical.

2. SOLUTE TRANSPORT AS A LINEAR DYNAMIC PROCESS

2.1. *Soil as a Dynamic System*

Conceptually, the soil between two points in the system (e.g., between two wells or piezometers in the field or between the inlet and outlet of a soil column in the laboratory) can be viewed as a reactor through which water flows during saturated or unsaturated conditions. Unlike most chemical reactors, water flow in soil is generally transient and usually subject to relatively complicated time-dependent boundary conditions. In spite of this, current approaches require simplifying assumptions to study the behavior and transport of linearly interacting solutes, to compare experiments under different flow conditions, and to evaluate the basic physicochemical processes affecting water and solute transport. As such, we assume that (1) water flow is steady and macroscopically deterministic, (2) the soil system consists of an isolated stream tube bounded by one inlet and one outlet cross section through which water flows solely by convection, (3) there are no sources or sinks for water inside the stream tube, and (4) inlet and outlet concentrations are flux averaged. These assumptions are needed to accurately define the residence time distribution below and are easily satisfied when carrying out laboratory soil column displacement experiments. Note that assumption 2 means that there is no dispersion at the inlet and outlet boundaries, whereas assumption 4 implies that the inlet and outlet concentrations are averaged with respect to the velocity field only. The mathematical formulation of these two assumptions are discussed in detail in section 3.1.

Any concentration signal $y(t)$ at the inlet as a function of time t is assumed to start at time $t = 0$ and is taken to be zero for negative time. This definition can always be made valid for a linear system by shifting the time or the initial concentration level. The inlet cross section is located at point 0 and the outlet cross section at point L. Let $y(0, t)$ be the flux-averaged concentration signal of a solute injected at point 0 and $y(L, t)$ the associated time response at point L. A system is said to be linear when the response to a linear combination of $y_i(0, t)$ is the same linear combination of the individual responses $y_i(L, t)$. The main task of linear system dynamics is to formulate possible relationships between $y(0, t)$ and $y(L, t)$. This is done most conveniently with the help of transfer functions. To derive a transfer function, let us define the Laplace transform, $\bar{y}$, of the signal y, as follows:

$$\bar{y}(0, s) = \int_0^\infty y(0, t)e^{-st}\, dt \tag{1}$$

$$\bar{y}(L, s) = \int_0^\infty y(L, t)e^{-st}\, dt \tag{2}$$

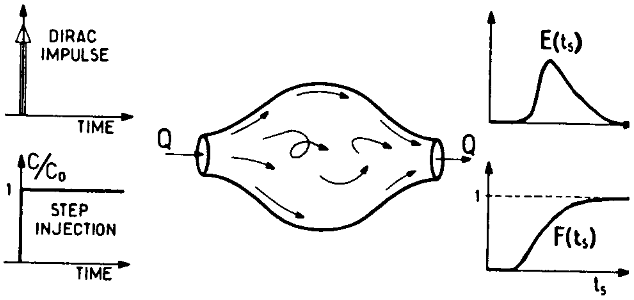

Fig. 1. Schematic of a soil system, with input signals, $E(t_s)$ and $F(t_s)$.

where s is the Laplace variable. The transfer function $G(L, s)$ of the soil system is defined by [*Wen and Fan*, 1975]:

$$G(L, s) = \frac{\bar{y}(L, s)}{\bar{y}(0, s)}. \tag{3}$$

We will show that $G(L, s)$ is independent of the input and output signals and hence completely characterizes the transient behavior of the system. For notational convenience we will omit the variable L in $G(L, s)$ when no confusion is possible.

Other transfer functions will be presented also. Similarly as (3), they are defined by the ratio of two concentrations in the Laplace domain.

2.2. *The Residence Time Distribution*

Consider a soil system (Figure 1) with constant volumetric flow rate Q. The residence time t_s of a water molecule is the time needed for the molecule to travel from the inlet to the outlet cross section. If we instantaneously inject a given amount (n_0) of a perfect tracer for water (no interaction with the solid phase) at the inlet of a tracer-free soil system, and if $y(L, t)$ is the flux-averaged response at the outlet, then $Qy(L, t)\, dt$ is the amount of tracer which stayed in the soil system for a small time period dt between times t and $t + dt$. The residence time distribution (RTD) [*Dankwerts*, 1953] of the tracer is obtained upon normalizing Qy, and substituting the residence time t_s for t,

$$E(t_s) = \frac{Qy(L, t_s)}{\int_0^\infty Qy(L, t_s)\, dt_s} = y(L, t_s)\,\frac{Q}{n_0} \tag{4}$$

so that, by definition,

$$\int_0^\infty E(t_s)\, dt_s = 1. \tag{5}$$

The right-hand side of equality (4) enables one to estimate Q from knowledge of $C(L, t_s)$ and n_0. Since an ideal tracer is assumed to behave as water, $E(t_s)$ is the RTD of water. By definition the RTD is the outlet concentration response of the system to a Dirac delta input function $\delta(t)$ for an ideal tracer. Using (3) and the Laplace transform of $\delta(t)$, the transfer function of the soil system, $G(s)$, i.e., the Laplace transform of $E(t_s)$, gives

$$G(s) = \int_0^\infty E(t)e^{-st}\, dt. \tag{6}$$

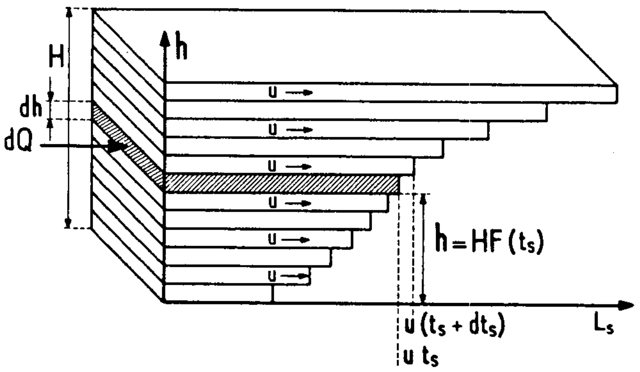

Fig. 2. Schematic of the "bundle of parallel tubes" model. The tubes have a length proportional to the residence time. The feed flow rates dQ to the tubes are chosen such that they give the desired RTD. Plug flow at the same velocity, u, prevails in the tubes.

The step response $F(t_s)$ is the response to a unit step Heaviside function $H(t)$ such that $y(0, t) = H(t)$. Since $H(t)$ is the integral of $\delta(t)$ and the tracer behaves linearly, $F(t_s)$ and $E(t_s)$ are related by

$$F(t_s) = \int_0^{t_s} E(t)\, dt. \tag{7}$$

Hence the Laplace transform of $F(t_s)$ is

$$\bar{F}(s) = \frac{G(s)}{s}. \tag{8}$$

A schematic of the RTD is given by the "bundle of parallel tubes" model in Figure 2. The flow system is assumed to consist of a set of parallel tubes of rectangular cross section of the same width. Piston (or plug) flow occurs in each tube at the same velocity u. The total height of the bundle is H. The length and thickness of each tube, as well as its feed flow rate, are chosen such that their ensemble gives the desired RTD. *Villermaux* [1982] has shown that a tube with a residence time between t_s and $t_s + dt_s$ has a length $L_s = ut_s$, a thickness $dh = HE(t_s)\, dt_s$, and is fed at a flow rate $dQ = QE(t_s)\, dt_s$. When the height of the bundle is normalized by H and the length of the tubes by u, the envelope of the tube outlets is $F(t_s)$. From this simple picture, $E(t_s)\, dt_s$ may be viewed as the fraction dQ/Q of the flow rate composed of fluid molecules having a residence time between t_s and $t_s + dt_s$.

2.3. *Moments of the RTD*

Properties of the RTD can be described by time moments. The kth-order moment is

$$\mu_k = \int_0^\infty t^k E(t)\, dt \tag{9}$$

For instance, the first-order moment, or mean residence time $\bar{t}_s$, is given by

$$\mu_1 = \bar{t}_s = \int_0^\infty tE(t)\, dt. \tag{10}$$

Central moments are defined by

$$\mu_k' = \int_0^\infty (t - \bar{t}_s)^k E(t)\, dt \tag{11}$$

which, for example, leads to the second central moment, or variance σ^2,

$$\sigma^2 = \mu_2' = \mu_2 - \mu_1^2 = \int_0^\infty (t - \bar{t}_s)^2 E(t)\, dt. \tag{12a}$$

The reduced variance σ'^2 is defined as

$$\sigma'^2 = \frac{\sigma^2}{\bar{t}_s^2} \tag{12b}$$

According to (7), $E(t) = dF/dt$, and (10) and (12a) give for a step response

$$\mu_1 = \bar{t}_s = \int_0^\infty [1 - F(t)]\, dt \tag{13}$$

$$\sigma^2 = 2 \int_0^\infty [1 - F(t)]t\, dt - \bar{t}_s^2 \tag{14}$$

Regardless of the transport model to be used, the first-order moment gives an estimate of the volume, V_a, of the porous medium that is accessible to the fluid. When the flow across the inlet and outlet boundaries occurs by convection only (see assumption 2, section 2.1), it can be shown that [*Villermaux*, 1982]:

$$\mu_1 = \bar{t}_s = \frac{V_a}{Q} \tag{15}$$

The use of higher-order moments, leading to the "skewness" (third order) and "kurtosis" (fourth order) of the RTD, generally does not improve the accuracy of the analysis because of increased statistical weight of noisy experimental data in the tails of the distribution.

2.4. *Properties of Transfer Functions*

Knowledge of the transfer function $G(s)$ enables one to calculate the response of a soil system to an arbitrary input $y(0, t)$ by making use of (3) and inverting the Laplace transform of the response using either analytical or numerical techniques. This means that a dynamic system is completely characterized by its transfer function. Hence we will focus our attention primarily on $G(s)$.

Subsystems are considered to be in series when the output variable of one subsystem is the input variable to the next subsystem. From (3) it follows that the overall transfer function of N subsystems in series is the product of the transfer functions $G_j(s)$ of each subsystem, i.e.,

$$G(s) = \prod_{j=1}^{N} G_j(s) \tag{16}$$

Theoretical expressions for the moments may be deduced from knowledge of $G(s)$. Comparing (6) and (9), one obtains by differentiation with respect to s

$$\mu_k = (-1)^k \left(\frac{\partial^k G}{\partial s^k}\right)_{s=0} \tag{17a}$$

For an arbitrary transfer function $G(s)$, which is not the Laplace transform of a normalized function, $G(0)$ is the zeroth-order moment which must be used to normalize the function. For instance, (1) shows that $\bar{y}(0, 0)$ is the normalizing factor of $y(0, t)$. Then, the kth-order moments of the normalized function are given by

$$\mu_k = \frac{(-1)^k}{G(0)} \left(\frac{\partial^k G}{\partial s^k}\right)_{s=0} \tag{17b}$$

Equations (17*a*) and (17*b*) may be used to calculate the time moments without having to invert the transfer function.

Applying (17*b*) to $\bar{y}(0, s)$ and $\bar{y}(L, s)$, and using (3), the mean and variance of the RTD can be deduced from the means and variances of the input and output signals, respectively:

$$\bar{t}_s = \bar{t}(L) - \bar{t}(0) \tag{18a}$$

$$\sigma^2 = \sigma^2(L) - \sigma^2(0) \tag{18b}$$

For systems in series as defined above the mean residence time and the variance of the overall transport system is equal to the sum of the mean residence times and variances of each subsystems, respectively. We emphasize that this last property of systems in series, as well as (15), (16), (18*a*) and (18*b*) are valid only if assumptions 2 and 4 of section 2.1 are fulfilled.

3. SOLUTE TRANSPORT MODELS

Two types of models may be used for predicting solute transport in porous media. Continuous models, especially popular in the soil and hydrological sciences, assume continuous spatial variations in solute concentrations, and often also in the water flow and solute interaction parameters. These types of models are expressed in the form of partial differential equations. Discrete (or lumped) parameter models, on the other hand, assume that spatial variations can be represented by a network of suitably connected subsystems, each one having its own properties. The basic subsystem is a "continuous stirred reactor" or "mixing cell" of uniform composition. Hence the entire system can be modeled by a set of ordinary differential equations.

Before presenting a method for building a discrete transport model, we will show the equivalence between the continuous and discrete approaches using the problem of one-dimensional convective-dispersive transport of a nonreactive solute (ideal tracer) in an aggregated soil as an example. Convective-dispersive solute transport is assumed to be confined only to the mobile water phase, whereas solute transfer between mobile and immobile soil-water is assumed to be diffusion controlled [*Coats and Smith*, 1964].

3.1. *Continuous Models*

Let θ_m and θ_{im} be the volume fractions of mobile and immobile water, respectively. Deviations from ideal piston (plug) flow are often lumped into a macroscopically defined dispersive flux obeying Fick's law. This dispersive flux is superimposed on the convective flux vC_m where v is the pore water velocity and C_m the solute concentration in the mobile phase. The flow velocity v equals $Q/\Omega\theta_m$, where Ω is the total cross-sectional area. The mass balance equation for the mobile phase is [*Coats and Smith*, 1964; *van Genuchten and Wierenga*, 1976]:

$$\frac{\partial C_m}{\partial t} + \frac{\theta_{im}}{\theta_m}\frac{\partial C_{im}}{\partial t} = D\frac{\partial^2 C_m}{\partial x^2} - v\frac{\partial C_m}{\partial x} \tag{19}$$

where C_m is the resident concentration in the mobile liquid phase, C_{im} is the concentration in the immobile liquid phase, and D is the longitudinal hydrodynamic dispersion coefficient. The mass balance equation for solute in the immobile phase is

$$\theta_{im}\frac{\partial C_{im}}{\partial t} = k_M(C_m - C_{im}) \tag{20}$$

where k_M is a mass transfer coefficient. Equation (20) considers solute exchange between the mobile and immobile regions as a first-order dynamic process. Recalling that concentrations are assumed to be zero at $t = 0$, (20) becomes in the Laplace domain

$$\bar{C}_{im} = \frac{\bar{C}_m}{1 + st_M} \tag{21a}$$

$$t_M = \frac{\theta_{im}}{k_M} \tag{21b}$$

where t_M is a characteristic mass transfer time. A more general definition of t_M will be given in section 4. The transfer function $M(s)$ relating the amounts of solute in the two liquid phases is defined by

$$M(s) = \frac{\theta_{im}\bar{C}_{im}}{\theta_m\bar{C}_m} = \frac{K_{im}}{1 + st_M} \tag{22}$$

where $K_{im} = \theta_{im}/\theta_m$. Combining (22) and the Laplace transform of (19) yields

$$D\frac{d^2\bar{C}_m}{dx^2} = v\frac{d\bar{C}_m}{dx} + s[1 + M(s)]\bar{C}_m \tag{23}$$

Equation (23) may be solved for various boundary conditions. To obtain the RTD, we must assume that convection prevails at the inlet and outlet and that $y(0, t) = \delta(t)$ (Dirac input). Consequently, the boundary conditions in the Laplace domain are [*Wen and Fan*, 1975; *Nauman and Buffham*, 1983]:

$$v\bar{y}(0, s) = v\bar{C}_m(0^+, s) - D\frac{d\bar{C}_m(0^+, s)}{dx} \tag{24a}$$

$$\frac{d\bar{C}_m(L, s)}{dx} = 0 \tag{24b}$$

$$\bar{y}(0, s) = 1 \tag{24c}$$

$$\bar{y}(L, s) = \bar{C}_m(L, s) \tag{24d}$$

Equations (24*a*) and (24*b*) are the boundary conditions for the mass balance equation (23) in terms of the resident concentration C_m. Equation (24*c*) and (24*d*) define the flux-averaged concentrations y which are involved in the transfer function. Equation (24*a*) implies that the convective inlet flux, $vy(0, t)$, becomes a convective-dispersive flux as soon as the concentration signal enters the system. On the other hand, (24*b*) means that the dispersion flux vanishes at the outlet. The above equations assume that diffusion and dispersion in the inlet and outlet reservoirs upstream and downstream of the column is negligible. Solving (23) with boundary conditions (24*a*) and (24*b*), and using (3), (24*c*) and (24*d*) yields

$$G(s) = \frac{4q \exp\left[\frac{P}{2}(1-q)\right]}{(1+q)^2 - (1-q)^2 \exp(-Pq)} \tag{25a}$$

$$q = \left\{1 + 4t_m \frac{s[1 + M(s)]}{P}\right\}^{1/2} \tag{25b}$$

where $P = vL/D$ is the Péclet number and $t_m = L/v$ is the characteristic convection time in the mobile phase (i.e., the residence time for mobile water).

The mean residence time $\bar{t}_s$ and reduced variance σ'^2 are obtained from (17*a*), (22), and (25*a*) and (25*b*):

$$\bar{t}_s = t_m(1 + K_{im}) \tag{25c}$$

$$\sigma'^2 = \frac{\sigma^2}{\bar{t}_s^2} = \frac{2}{P} - \frac{2}{P^2}(1 - e^{-P}) + \frac{2K_{im}}{1 + K_{im}} \frac{t_M}{\bar{t}_s} \tag{25d}$$

Equation (25*c*) shows that the mean residence time $\bar{t}_s$ of the fluid is independent of the mass transfer kinetic and hydrodynamic dispersion processes. This feature is a consequence of assumptions 2 and 4 of section 2.1. The variance of the RTD is the sum of contributions resulting from hydrodynamic dispersion (first two terms of (25*d*)) and mass transfer kinetics (third term of (25*d*)). An increase in the mass transfer time t_M relative to the mean residence time $\bar{t}_s$ leads to additional spreading of the RTD.

Alternative expressions for the transfer function may be derived when boundary conditions other than (24) are chosen [*Wen and Fan*, 1975; *Villermaux*, 1981*a*, 1982; *Nauman and Buffham*, 1983]. *Van Genuchten and Parker* [1984] and *Van Genuchten and Wierenga* [1986] investigated the effects of different boundary conditions assuming instantaneous equilibrium between mobile and immobile water (i.e., $k_M \rightarrow \infty$). They showed that (25*c*) does not hold for some boundary conditions, especially when dispersion occurs upstream of the inlet or downstream from the outlet boundary. In these cases the solutions of (23) can be used for various purposes; however, they do not define the RTD.

For most experimental situations involving Péclet number greater than five, (25*d*) can be approximated closely by

$$\sigma'^2 = \frac{\sigma^2}{\bar{t}_s^2} = \frac{2}{P} + \frac{2K_{im}}{1 + K_{im}} \frac{t_M}{\bar{t}_s} \tag{25e}$$

3.2. *Discrete Models*

The soil is now represented by a cascade of J identical mixing cells of uniform composition. Each cell with volume V/J contains mobile and immobile water volumes of $\theta_m V/J$ and $\theta_{im} V/J$, respectively. The mass balance equations for the solute in the mobile and immobile water of cell j are, respectively,

$$QC_{m,j-1} = QC_{m,j} + \frac{\theta_m V}{J}\frac{dC_{m,j}}{dt} + \frac{\theta_{im} V}{J}\frac{dC_{im,j}}{dt} \tag{26}$$

$$j = 1, 2, \cdots, J$$

$$\theta_{im}\frac{dC_{im,j}}{dt} = k_M(C_{m,j} - C_{im,j}) \tag{27}$$

where $C_{m,j}$, is the solute concentration of the mobile water phase inside and at the outlet of cell j and $C_{im,j}$ is the associated concentration of the immobile water. Taking the Laplace transform of (26) and (27), and eliminating $C_{im,j}$, gives the transfer function $G_j(s)$ for cell j

$$G_j(s) = \frac{\bar{C}_{m,j}}{\bar{C}_{m,j-1}} = \left\{1 + \frac{st_m}{J}[1 + M(s)]\right\}^{-1} \tag{28}$$

Since convection prevails at the inlet and outlet boundaries, $C_{m,0} = y(0, t)$, and $C_{m,J} = y(L, t)$. Hence, substituting (28) into (16) yields the transfer function for the soil system as a whole:

$$G(s) = \frac{\bar{y}(L, s)}{\bar{y}(0, s)} = \frac{\bar{C}_{m,J}}{\bar{C}_{m,0}} = \prod_{j=1}^{J} G_j(s)$$

$$= \left\{1 + \frac{st_m}{J}[1 + M(s)]\right\}^{-J} \tag{29}$$

The moments of the RTD are again obtained with (17*a*):

$$\bar{t}_s = t_m(1 + K_{im}) \tag{30a}$$

$$\sigma'^2 = \frac{\sigma^2}{\bar{t}_s^2} = \frac{1}{J} + \frac{2K_{im}}{1 + K_{im}}\frac{t_M}{\bar{t}_s} \tag{30b}$$

Notice that (30*a*) and (25*c*) are identical and that (30*b*) and (25*d*) are of the same form. The term $1/J$ in the discrete model accounts for the effects of dispersion. Matching the variance of the discrete model (30*b*) with the variance of the continuous model (25*e*) shows that $P = 2J$. As long as P is greater than about 5 or 10, differences between the two models are generally less than the experimental errors [*Villermaux*, 1981*a*, 1982]. Therefore we will assume that both models are equivalent.

To compare the relative effects of dispersion (i.e., P or J), convection in mobile water (t_m), mass transfer limitations (t_M), and immobile/mobile water ratio (K_{im}) on solute transport, it is convenient to introduce a characteristic dispersion time t_D in the reduced variance as follows:

$$\sigma'^2 = \frac{2}{t_m}(t_D + t'_M) \tag{31a}$$

where

$$t'_M = \frac{K_{im}}{(1 + K_{im})^2} t_M \tag{31b}$$

Comparing (31*a*) and (25*e*) gives

$$t_D = \frac{D}{v^2} = \frac{t_m}{P} \tag{32a}$$

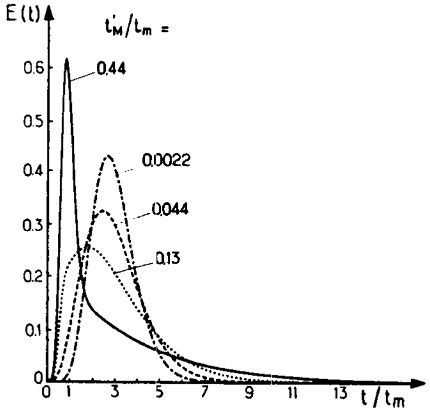

Fig. 3. Breakthrough curves calculated with the mixing-cell-in-series model, assuming J = 10 (P = 20, t_D/t_m = 0.05), K_{im} = 2, and several values for t'_M/t_m. For $t'_M/t_m \leq 2.2\ 10^{-3}$, all curves are superimposed. All BTCs have the same mean retention time $\bar{t}_s$ = $3t_m$.

For the discrete model, (31a) and (30b) give

$$t_D = \frac{t_m}{2J} \tag{32b}$$

It is now possible to define two main transport regimes. When $t'_M \gg t_D$, mass transfer kinetics between the mobile and immobile regions is the predominant process for broadening the RTD. On the other hand, when $t_D \gg t'_M$, hydrodynamic dispersion becomes the predominant broadening process. In the latter case the local equilibrium assumption (LEA) holds, since mass transfer resistance is now effectively blurred by dispersion.

The influence of mass transfer kinetics is illustrated in Figure 3 which shows breakthrough curves (BTCs) for a Dirac injection of a tracer with J = 10 (i.e., P = 20 or t_D/t_m = 0.05) and K_{im} = 2. The BTCs in the real time domain were computed using a fast Fourier transform algorithm to invert $G(s)$ [*Brigham*, 1974]. As long as $t'_M \ll t_D$, RTDs are superimposed and remain almost symmetrical. The larger the Péclet number, the more symmetrical the RTD. When $t'_M \approx t_D$, the RTD broadens and also loses its symmetrical shape. When $t'_M \gg t_D$, the RTD is even broader than before and becomes quite asymmetrical. Finally, when $t_M \gg t_m$, the RTD is extremely asymmetrical and composed of a solute peak located at $t = t_m$ and a long skewed tail. This shows that lumping both hydrodynamic dispersion and mass transfer processes into a "limiting dispersion coefficient" can be a dangerous simplifying approach. Similar results were obtained earlier by *van Genuchten and Wierenga* [1976]. We conclude that a comparison of the characteristic times t_m, t'_M, and t_D is a powerful method for isolating the predominant processes responsible for the shape of the RTD.

Having established the equivalence of the continuous and discrete models, we will now use only the discrete model to simulate the convective-dispersive transport of solutes with mass transfer kinetics. The discrete model is much easier to work with than the continuous model, avoids boundary condition problems and, as shown below, can also simulate any flow pattern by making a suitable choice of cell volumes and connections between cells.

4. A GENERAL METHOD FOR BUILDING SOLUTE TRANSPORT MODELS

We now present a powerful method for modeling transpor in more complex systems which involve also adsorption o the solute by the solid phase. The method is based on progressively building up $G(s)$ from knowledge of transfer functions that describe solute behavior at the local (microscopic) level. Because adsorption of the solute on the solid matrix causes the mean residence times of water and the solute to be different, the mean residence time of the solute will be called the mean retention time and denoted t_r.

First, we decouple transport in the mobile water phase from mass transfer toward the stationary phase using a theorem presented by *Villermaux* [1973]. If $G_m(s)$ is the Laplace transform of the RTD, $E_m(t)$, of a nonreactive solute in the mobile phase, and if $M(s)$ is the transfer function relating the local amounts of solute in the mobile and stationary phases (the latter consisting of immobile water and the adsorbing soil matrix), then the overall transfer function $G(s)$ describing the simultaneous contributions of transport, mass transfer, and adsorption, is given by

$$G(s) = G_m(s_1) \tag{33a}$$

$$s_1 = s[1 + M(s)] \tag{33b}$$

where (see also (22)):

$$M(s) = \frac{\bar{n}_{im}(s) + \bar{n}_a(s)}{\bar{n}_m(s)} \tag{34}$$

in which $\bar{n}_{im}(s)$, $\bar{n}_m(s)$, and $\bar{n}_a(s)$ denote the solute masses (in the Laplace domain) in the immobile water phase, the mobile water phase, and adsorbed on the solid phase, respectively. These amounts are defined for an elementary volume dV in the continuous model and for the volume of a cell in the discrete model. Equations (33) suggest that mass transport in the mobile phase, i.e., $G_m(s)$, and the adsorption and mass transfer processes, i.e., $M(s)$, can be studied independently. Also, notice that (25a) and (25b), and (29) are special cases of (33). In (29), $G_m(s)$ is of the form

$$G_m(s) = \left(1 + \frac{st_m}{J}\right)^{-J} \tag{35}$$

The decoupling property (33) is based on the bundle-of-parallel-tubes model of Figure 2, and assumes that the mass transfer coefficient and the sorbing capacity of the stationary phase are constant, and independent of the tube length. Recent studies of gaseous diffusion in porous catalysts suggest that this may not always be true [*Cui et al.*, 1990]. We nevertheless assume for now that (33) is valid.

Applying (17a) to (33) yields an expression for the mean retention time of the retarded solute:

$$\mu_1 1 = t_r = t_m[1 + M(0)] = t_m[1 + K'] \tag{36}$$

We show in the appendix that the substitution $s = 0$ in a transfer function yields a ratio of two variables at steady state ($t \rightarrow \infty$). In this case, $M(0)$ is the ratio of the amounts of solute in the stagnant and mobile regions at steady state. Provided there are no chemical reactions, this ratio depends on the equilibrium properties of the medium and is independent of any kinetic or dispersion parameter. Thus (36) implies that the first-order moment does not depend on any dispersion and mass transfer parameters. Below we shall use K' for $M(0)$. In chromatography, K' is often called the capacity factor.

The second derivative of $G(s)$ gives the expression for the reduced variance,

$$\sigma'^2 = \frac{\sigma^2}{t_r^2} = \sigma_m'^2 - \frac{2M'(0)}{1+K'}\frac{1}{t_r} \tag{37}$$

where $\sigma_m'^2$ is the variance of $E_m(t)$ normalized by t_r^2, and $M'(0) = [dM(s)/ds]_{s=0}$. Introducing the first-order moment t_M of $M(s)$ given by (17b), one obtains

$$t_M = -M'(0)/M(0) = -M'(0)/K' \tag{38}$$

$$\sigma'^2 = \sigma_m'^2 + \sigma_{im}'^2 \tag{39a}$$

$$\sigma_{im}'^2 = \frac{2K'}{1+K'}\frac{t_M}{t_r} = \frac{2K'}{(1+K')^2}\frac{t_M}{t_m} = 2\frac{t_M'}{t_m} \tag{39b}$$

$$t_M' = \frac{K'}{(1+K')^2}t_M \tag{39c}$$

where $\sigma_{im}'^2$ is the reduced variance for the stationary phase. Equations (39a) and (39b) indicate that the contributions of transport in the mobile water phase (i.e., $\sigma_m'^2$) and mass transfer kinetics (i.e., $\sigma_{im}'^2$) are additive in the total variance, irrespective of the type of process responsible for mass transfer and deviations from piston flow in the mobile water phase. Notice that no assumptions are made concerning $E_m(t)$ or $G_m(s)$, and hence that $\sigma_m'^2$ can account for band-spreading processes due to flow patterns other than hydrodynamic dispersion. Equations (30b), (25d), and (25e) are simple cases of the more general equations (39a), whereas (38) generalizes the characteristic mass transfer time t_M defined by (21b). In the next two sections we shall decompose K', t_M, and $G_m(s)$ into several elementary contributions. In section 5 we focus on the description of mass transfer at the local level, i.e., on methods to obtain $M(s)$. In section 6 we discuss a method for building the overall transfer function $G_m(s)$ for an arbitrary network representing transport in mobile and immobile water.

5. Mass Transfer Kinetics and Interactions at the Local Level

Consider an aggregate as an elementary entity composed of a porous solid matrix containing immobile water, and around which water flows. For the discrete model above we considered only two description levels: the mobile region characterized by $G_m(s)$ and the immobile region characterized by a first-order system $M(s)$. In general, it is possible to distinguish several sublevels with multiple interactions responsible for the transient behavior of the immobile region. For instance, mass transfer to a porous aggregate has traditionally been described by two different processes in series: external diffusion in the viscous boundary layer around the aggregate, and internal diffusion inside the aggregate (Figure 4a). Moreover, when solute adsorbs, internal diffusion is coupled with adsorption kinetics. The question is hence how to combine these two individual processes? By using a linearly adsorbing solute as an example, we will illustrate the method for progressively building the function $M(s)$ and discuss limitations and advantages of some simplified approaches.

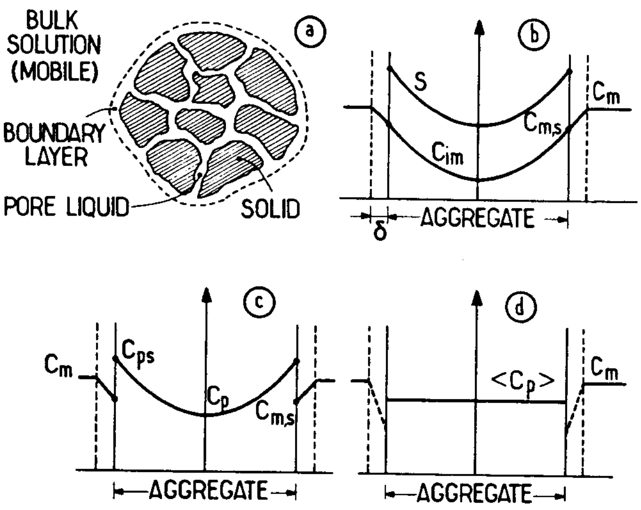

Fig. 4. Schematic of an aggregate (a) showing possible solute distributions (b) for a two-phase model in which concentrations depend upon the position, (c) in an aggregated, equivalent homogeneous medium with nonuniform composition, and (d) in an equivalent homogeneous medium with uniform solute distribution where concentrations are averaged over the aggregate volume. The coefficient δ is the thickness of the viscous boundary layer.

At least three approaches are possible for describing the physicochemical composition of the aggregate conceptually (Figure 4). One approach (Figure 4b) could consider the aggregate as a continuous two-phase porous medium with a uniform physical composition and a nonuniform composition with respect to the solute. The local solute concentration of the pore liquid of the aggregate (the immobile region), C_{im}, is defined as the mass of solute per unit volume of pore water. The concentration of solute adsorbed on the solid matrix S is defined as the mass of solute per unit mass of solid. The solution and adsorbed concentrations are dependent on the position in the aggregate. Examples of this approach are given by *Rasmuson* [1985], and *Tang et al.* [1981].

One may also consider the aggregate as an equivalent homogeneous medium with nonuniform composition (Figure 4c). The interior of the aggregate is considered a single phase for which the local concentration of solute, C_p, is given by

$$C_p = \beta_{im}C_{im} + \rho_a S \tag{40}$$

where β_{im} is the volume of immobile water per unit volume of aggregate and ρ_a is the bulk density of the aggregate. If linear and instantaneous liquid/solid equilibrium prevails, $S = K_a C_{im}$, and (40) becomes

$$C_p = C_{im}(\beta_{im} + \rho_a K_a) = \alpha C_{im} \tag{41}$$

At equilibrium, $C_{im} = C_m$, which shows that α is a distribution coefficient between mobile water and the aggregate.

A third approach (Figure 4d) results when the aggregate is viewed as an equivalent medium of uniform composition in which the concentrations $\langle C_{im}\rangle$, $\langle S\rangle$, and $\langle C_p\rangle$ are defined by averaging the local concentrations C_{im}, S, and C_p over the aggregate volume. Equation (40) then becomes

$$\langle C_p\rangle = \beta_{im}\langle C_{im}\rangle + \rho_a\langle S\rangle \tag{42a}$$

If adsorption is instantaneous and recalling that the physical composition of the aggregate is uniform, ($42a$) reduces to

$$\langle C_p\rangle = \alpha\langle C_{im}\rangle \qquad (42b)$$

The aggregate may now be viewed as a dynamic system characterized by a transfer function $M(s)$ defined by (34). Let $1 - \varepsilon_m$ be the volumetric fraction of aggregates relative to the whole soil system. $M(s)$ is given by

$$M(s) = \frac{1-\varepsilon_m}{\theta_m} L(s) \qquad (43a)$$

$$L(s) = \frac{\overline{\langle C_p\rangle}}{\bar{C}_m} \qquad (43b)$$

At equilibrium, $C_m = C_{im} = \langle C_{im}\rangle$, and $L(0)$ becomes the ratio of $\langle C_p\rangle$ to C_m in the real time domain (see appendix). From ($42b$) it follows that $L(0)$ is equal to the distribution coefficient α.

5.1. *External Mass Transfer Resistance With Instantaneous Adsorption*

The rate of external mass transfer is determined by the manner in which laminar flow in the viscous boundary layer is coupled with the transverse diffusive mass transfer process. A detailed description of this coupling at the microscopic level is extremely complicated, and some approximate approach is required in practice. In the "film model" [*Levenspiel*, 1972; *Froment and Bischoff*, 1979; *Villermaux*, 1982; *Aris*, 1975], the specific flux of solute, q_s, across the boundary layer is given by

$$q_s = D_{\text{mol}} \frac{C_m - C_{m,s}}{\delta} = k_e(C_m - C_{m,s}) \qquad (44)$$

where $C_{m,s}$ is the concentration of the mobile water at the aggregate boundary, D_{mol} is the ionic or molecular diffusion coefficient in the liquid phase, δ is the thickness of the viscous boundary layer, and $k_e = D_{\text{mol}}/\delta$ is the external mass transfer coefficient. Note that k_e (or δ) is generally obtained from empirical correlations [*Levenspiel*, 1972; *Froment and Bischoff*, 1979; *Villermaux*, 1982; *Crittenden et al.*, 1986]. Although (44) is theoretically valid only at steady state, many experiments suggest that the equation also holds for transient conditions. As with most authors, we assume that (44) also holds for transient conditions, even though the assumption itself remains debatable. Finally, we mention that $C_{m,s}$ is still an undefined concentration which eventually depends on the processes taking place inside the particle.

Matching the solute flux through the external aggregate surface with the total solute accumulation in the aggregate leads to the following balance equation:

$$\frac{D_{\text{mol}}}{\delta} S_p(C_m - C_{m,s}) = V_p \frac{d\langle C_p\rangle}{dt} \qquad (45)$$

where S_p is the external surface area of the aggregate and V_p the volume of the aggregate. Using ($42b$), (45) can be rearranged as

$$C_m = C_{m,s} + \alpha \frac{\delta l}{D_{\text{mol}}} \frac{d\langle C_{im}\rangle}{dt} \qquad (46)$$

where $l = V_p/S_p$ is the characteristic length of the aggregate. Let us introduce the characteristic external mass transfer time t_e:

$$t_e = \alpha \frac{\delta l}{D_{\text{mol}}}. \qquad (47)$$

The Laplace transform of (46) is

$$\bar{C}_m = \bar{C}_{m,s} + t_e s \overline{\langle C_{im}\rangle}. \qquad (48)$$

Let us also introduce the transfer function $H(s)$ defined by

$$H(s) = \frac{\overline{\langle C_{im}\rangle}}{\bar{C}_{im,s}} \qquad (49)$$

where $C_{im,s}$ is the concentration of solute in the immobile water phase at the aggregate boundary. $H(s)$ relates, in the Laplace domain, the average concentration of the immobile fluid with the concentration at the aggregate boundary. This transfer function, which depends exclusively on the internal mass transfer process and adsorption equilibrium processes inside the aggregate, will be discussed in more detail in the next two sections. At the aggregate boundary the solute concentrations in the pore water ($C_{im,s}$) and in the external fluid ($C_{m,s}$) must be related in some fashion. This relationship will implicitly define the concentration $C_{m,s}$ in the film model. For the sake of simplicity we assume continuity of the concentration in the internal and external liquid phases, i.e.,

$$C_{m,s} = C_{im,s} \qquad (50)$$

Other assumptions could also be made. For instance, when the solute is an anion in an aggregated fine-textured soil, $C_{im,s}$ may becomes smaller than $C_{m,s}$ because of anion exclusion, in which case there is no longer concentration continuity.

Combination of (41), ($43a$), ($43b$), (48), (49), and (50) gives finally the transfer function for exchange between the mobile phase and the aggregate, i.e.,

$$M(s) = \frac{\alpha(1-\varepsilon_m)}{\theta_m} \frac{1}{\dfrac{1}{H(s)} + st_e} = K'\left[\frac{1}{H(s)} + st_e\right]^{-1} \qquad (51)$$

Equation (51) shows $M(s)$ consists of contributions from the viscous boundary layer (i.e., t_e) and the internal kinetic mass transfer process (i.e., $H(s)$). Using (41), the capacity factor K' is given by

$$K' = \frac{\alpha(1-\varepsilon_m)}{\theta_m} = K_{im} + \frac{1-\varepsilon_m}{\theta_m} \rho_a K_a \qquad (52a)$$

$$K_{im} = \frac{\beta_{im}(1-\varepsilon_m)}{\theta_m} = \frac{\theta_{im}}{\theta_m} \qquad (52b)$$

which clearly shows the contributions by immobile water in the aggregate (K_{im}) and adsorbed solute on the solid phase (K_a).

Assuming equality (50) holds, (51) is the most general transfer function independent of the type of internal diffusion process that may occur in the aggregate when adsorption is at equilibrium. This means that any internal diffusion model (i.e., $H(s)$) can now be used in conjunction with (51). Next

TABLE 1. Expressions for $H^*(s_2)$ for Several Aggregate Shapes in Terms of the Modified Laplace Transform Parameter $s_2 = l(s/D'_e)^{1/2}$

Aggregate Shape	Characteristic Length l	$H^*(s_2)$	Shape Factor μ
Slab, thickness $2l$	l	$\dfrac{\tanh s_2}{s_2}$	1/3
Infinite cylinder, radius r	$r/2$	$\dfrac{I_1(2s_2)}{s_2 I_0(2s_2)}$ [a]	1/2
Sphere, radius r	$r/3$	$\dfrac{\operatorname{cotanh}(3s_2)}{s_2} - \dfrac{1}{3s_2^2}$	3/5
Equivalent first order system	l	$\dfrac{1}{1+\mu s_2^2}$	μ

[a] I_0 and I_1 are zero- and first-order modified Bessel functions for the first kind.

we will describe the most classical case of internal and external diffusion with instantaneous adsorption in the aggregate.

5.2. *Internal and External Diffusion With Instantaneous Adsorption*

Assuming that adsorbed ions or molecules are motionless, the specific flux of internal mass transfer per unit area of aggregate surface q_s is given by Fick's law [*Aris*, 1975]:

$$q_s = -D_e \nabla C_{im} \tag{53}$$

where ∇ is the gradient operator and D_e an effective diffusion coefficient given by

$$D_e = \frac{\beta_{im}}{\tau} D_{\text{mol}} \tag{54}$$

where τ is the tortuosity factor for the aggregate ($1 < \tau < 5$ according to *Satterfield* [1970]). The local mass balance equations for the solute in the aggregate in the real time and Laplace domains are

$$\frac{\partial C_p}{\partial t} = \alpha \frac{\partial C_{im}}{\partial t} = D_e \nabla^2 C_{im} = \alpha D'_e \nabla^2 C_{im} \tag{55a}$$

$$s\bar{C}_p = \alpha s \bar{C}_{im} = D_e \nabla^2 \bar{C}_{im} = \alpha D'_e \nabla^2 \bar{C}_{im} \tag{55b}$$

respectively, where ∇^2 is the Laplace operator and $D'_e = D_e/\alpha$ is an apparent effective diffusion coefficient. Equation (55*b*) can be solved in the Laplace domain to obtain the transfer function $H(s)$. Analytical solutions are also readily available from the literature for simple aggregate shapes both in the time domain [*Crank*, 1956] and the Laplace domain [*Villermaux*, 1981*a*]. The solutions are summarized in Table 1 in terms of a modified Laplace parameter s_2:

$$s_2 = l\left(\frac{\alpha s}{D_e}\right)^{1/2} = l\left(\frac{s}{D'_e}\right)^{1/2} \tag{56a}$$

and standard functions H^* such that

$$H(s) = H^*(s_2) \tag{56b}$$

Whatever the aggregate shape, $H(s)$ has a first-order moment t_{im} given by (17*a*):

$$t_{im} = \mu l^2 \alpha / D_e = \mu l^2 / D'_e \tag{57}$$

where μ is a shape factor (see Table 1) depending on the aggregate geometry. *Villermaux* [1981*a*, 1987] and *van Genuchten* [1985] have shown that the complex function $H(s)$ can often be approximated accurately by a first-order system:

$$H(s) \approx \frac{1}{1 + t_{im} s} \tag{58}$$

The apparent effective diffusion coefficient D'_e is given by

$$D'_e = \frac{D_e}{\alpha} = \frac{D_{\text{mol}}}{\tau} \frac{\beta_{im}}{\beta_{im} + \rho_a K_a} \tag{59}$$

Equation (59) shows that the stronger the solute is adsorbed (K_a increases), the slower the internal diffusion process becomes. This situation will be completely different when the adsorbed solute is free to diffuse on the solid matrix surface. Equation (55) must then be replaced by

$$\frac{\partial C_p}{\partial t} = \alpha \frac{\partial C_{im}}{\partial t} = D_e \nabla^2 C_{im} + \rho_a D_{es} \nabla^2 S$$

$$= (D_e + D_{es} \rho_a K_a) \nabla^2 C_{im} = \alpha D'_e \nabla^2 C_{im} \tag{60}$$

where D_{es} is an effective surface diffusion coefficient of the adsorbed ion or molecule. Equation (60) shows that D'_e is now given by

$$D'_e = \frac{D_e + D_{es} \rho_a K_a}{\beta_{im} + \rho_a K_a} = \frac{D_e + (\alpha - \beta_{im}) D_{es}}{\alpha} \tag{61}$$

Equation (61) indicates that D'_e approaches the nonzero limiting value D_{es} when K_a increases, whereas (59) results in a zero limiting value when K_a becomes large. We note that ion exchange at trace levels is generally a fairly linear adsorption process. Since adsorbed ions are only "trapped" in the electrical double layer of the liquid phase, *Nicoud and Schweich* [1989] suggested that they are still free to diffuse with $D_{es} \approx D_{\text{mol}}/\tau$. In that case, (61) reduces to

$$D'_e = \frac{D_{\text{mol}}}{\tau} = D_e \tag{62}$$

The importance of the mobility assumption becomes obvious when comparing (62) and (59). Even though the physical interpretation of D'_e depends on the mobility of the adsorbed solute, the final expression for $H(s)$ is fixed as soon as the aggregate shape is defined. For simplicity we shall assume below that adsorbed molecules are motionless; additional experimental evidence is necessary to validate this assumption.

Substituting one of the expressions for $H(s)$ in Table 1 in (51) gives the transfer function $M(s)$ for equilibrium adsorption.

5.3. *Internal and External Diffusion With Adsorption Kinetics*

Relatively little is known about the kinetics of adsorption in the liquid phase. Therefore we will adopt the simplest case of first-order kinetics. The local mass balance for the adsorbed phase is then

$$\frac{dS}{dt} = k_{\text{des}}(K_a C_{im} - S) \tag{63}$$

where k_{des} is a desorption rate constant. In the Laplace domain, (63) becomes

$$\bar{S}(s + k_{\text{des}}) = k_{\text{des}} K_a \bar{C}_{im} \tag{64}$$

Let us define the desorption time t_{des} by

$$t_{\text{des}} = \frac{\alpha - \beta_{im}}{\alpha k_{\text{des}}} \tag{65}$$

Combining (40) in the Laplace domain, (64) and (65) gives

$$\bar{C}_p = \frac{\alpha}{1 + A(s)} \bar{C}_{im} \tag{66a}$$

$$A(s) = \frac{s t_{\text{des}}}{1 + \dfrac{\beta_{im}}{\alpha - \beta_{im}} s t_{\text{des}}} \tag{66b}$$

Equation (66*a*) is similar to (41), except that (66*a*) is in the Laplace domain and that $\alpha/[1 + A(s)]$ is a transfer function which generalizes the distribution coefficient α by including first-order kinetics. The mass balance equations for the solute in the time and Laplace domain are now

$$\frac{\partial C_p}{\partial t} = D_e \nabla^2 C_{im} = \alpha D'_e \nabla^2 C_{im} \tag{67a}$$

$$s\bar{C}_p = \alpha \frac{s}{1 + A(s)} \bar{C}_{im} = D_e \nabla^2 \bar{C}_{im} = \alpha D'_e \nabla^2 \bar{C}_{im} \tag{67b}$$

respectively. Assuming that $A(s)$ does not depend on position inside the aggregate, a comparison of (67*b*) and (55*b*) indicates that $H(s)$ can now be derived in the same manner as in the previous section, except that s must be replaced by $s/[1 + A(s)]$. From (56*a*) it is thus sufficient to substitute $s/[1 + A(s)]$ for s to obtain:

$$\frac{\overline{\langle C_{im} \rangle}}{\bar{C}_{im,s}} = H(s) = H^*(s_3) \tag{68a}$$

$$s_3 = l \left\{ \frac{s}{D'_e[1 + A(s)]} \right\}^{1/2} \tag{68b}$$

where $H^*(s_3)$ is one of the functions given in Table 1, after substitution of s_2 for s_3. Similarly as for (51), $M(s)$ results from combining equations (43*a*), (43*b*), (48), (50), (67), (68*a*), (68*b*) to yield

$$M(s) = K' \left[\frac{1 + A(s)}{H^*(s_3)} + s t_e \right]^{-1} \tag{69}$$

Equation (69) is the most general transfer function and accounts for external diffusion (i.e., t_e), internal diffusion (i.e., $H^*(s_3)$), and first-order sorption kinetics (i.e., $A(s)$). When one of these processes is negligible or absent, the particular transfer function $M(s)$ is obtained by setting the associated characteristic time to zero. For instance, (69) reduces to (51) when $t_{\text{des}} = 0$ (i.e., $A(s) = 0$ and $s_3 = s_2$).

The overall characteristic mass transfer time t_M is obtained by applying (17*b*) to (69):

$$t_M = t_e + t_{im} + t_{\text{des}} \tag{70}$$

which shows that the characteristic times are additive, even though external diffusion, internal diffusion, and adsorption kinetics are coupled.

Generally, $M(s)$ has a rather complex mathematical structure owing to the form of $H(s)$. Equation (70) allows one to approximate $M(s)$ by a simple first-order transfer function $N(s)$ with the same zero and first-order moments:

$$N(s) = \frac{K'}{1 + s t_M} \tag{71}$$

Notice that when internal diffusion is not a limiting process, $t_{im} = 0$ and $H(s) = 1$, and hence $M(s) = N(s)$. *Villermaux* [1981*a*, 1987], *Rao et al.* [1980], and *van Genuchten* [1985] have shown that $N(s)$ is generally a good approximation for $M(s)$, except when t_{im} is the main contributor to t_M, and t_M is greater than t_m. This explains the popularity of the Coats and Smith model for which $M(s)$ reduces to $N(s)$ ((22) without adsorption). The development above shows that the characteristic time t_M in the Coats and Smith model is a lumped parameter which accounts for several different physical processes. Attempts to correlate the overall mass transfer time t_M to certain experimental parameters, such as aggregate size l or volumetric flow rate Q, will be extremely difficult and likely fail as pointed out by *Nkedi-Kizza et al.* [1983]. The same authors [*Nkedi-Kizza et al.*, 1984] also showed the equivalence of two models describing physical and chemical nonequilibrium. The controlling step was diffusional mass transfer (described by a first-order system) in the one model and kinetic adsorption in another model. Although their models accounted for parallel sorption sites in terms of a "two-site" model (to be discussed in section 5.6.), the equivalence resulted from the fact that both models involved the same transfer function $M(s) = N(s)$. The models differed only in the physical interpretation of t_M. In a different approach, *Crittenden et al.* [1986] studied the parameter sensitivity of a detailed model for linear solute transport. Most of their conclusions about the interdependence of various kinetic processes and associated parameters must be attributed to the fact that a given t_M may account for conceptually different transfer processes.

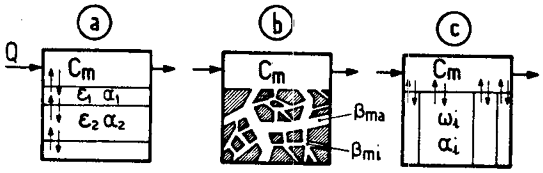

Fig. 5. Possible models for aggregates having nonuniform structure in a mixing cell: (*a*) retention sites in series, (*b*) two porosity levels, and (*c*) retention sites in parallel.

Until now, we have assumed that the aggregates are identical and have a uniform structure. This assumption is not always necessary. Models for $M(s)$ are also available for the following situations: (1) the aggregates are identical and composed of several layers in series, with each layer having its own properties (retention sites in series), (2) the aggregates are identical and have two embedded porosity levels, and (3) the aggregates are uniform and of the same geometry but with different properties which are distributed either continuously or discontinuously (retention sites in parallel). *Villermaux* [1981*a*, 1987] treated these three situations with considerable detail. We shall briefly discuss here the main results.

5.4. *Retention Sites in Series*

The aggregates consist of a series of n "concentric" layers with volume fraction ε_i relative to the volume of the aggregates and the mobile water phase, such that $\Sigma\varepsilon_i = 1 - \varepsilon_m$. We consider each layer as an equivalent medium with uniform composition and subject to instantaneous sorption. Figure 5*a* schematically shows the position of the layers in a mixing cell. The distribution coefficient, α_i, of the solute in layer i is defined as the ratio of the average total concentrations $\langle C_{p,i-1}\rangle$ and $\langle C_{p,i}\rangle$ of solute in layer $i - 1$ and i, respectively,

$$\alpha_i = \left(\frac{\langle C_{p,i}\rangle}{\langle C_{p,i-1}\rangle}\right)_{eq} \tag{72}$$

where the subscript eq indicates equilibrium. For $i = 0$, $\langle C_{p,0}\rangle = C_m$. Equation (72) generalizes (42*b*) which relates the concentration at a certain sublevel to the concentration at the immediately higher level. The mass transfer flux from layer $i - 1$ to layer i is given by $k_i(\langle C_{p,i-1}\rangle - \langle C_{p,i}\rangle/\alpha_i)$ which, as before, assumes that mass transfer kinetics can be modeled as a first-order process.

Let us introduce the characteristic mass transfer times τ_i as follows:

$$\tau_i = \frac{\alpha_i l_i}{k_i} \tag{73}$$

where l_i is the ratio of the volume of the entire aggregate to the exchanging surface area between layers i and $i - 1$. Equation (73) is similar to (57) and (47) if D_e/l and D_{mol}/δ in these two equations are considered to be mass transfer rate constants. The mass balance equation for the solute in layer i is

$$\varepsilon_i \frac{d\langle C_{p,i}\rangle}{dt} = \frac{\alpha_i\langle C_{p,i-1}\rangle - \langle C_{p,i}\rangle}{\tau_i} - \frac{\alpha_{i+1}\langle C_{p,i}\rangle - \langle C_{p,i+1}\rangle}{\tau_{i+1}} \tag{74}$$

A straightforward but tedious derivation based on the mass balance equations for each layer leads to the following relationships:

$$M(s) = \left(s\tau_1 \frac{\theta_m}{\alpha_1} + \Lambda_1(s)\right)^{-1} \tag{75a}$$

$$\frac{1}{\Lambda_i(s)} = \frac{\alpha_i\varepsilon_i}{\varepsilon_{i-1}}\left\{1 + \left[\frac{\varepsilon_i\tau_{i+1}}{\alpha_{i+1}} s + \Lambda_{i+1}(s)\right]^{-1}\right\} \tag{75b}$$

$$\frac{1}{\Lambda_n} = \frac{\alpha_n\varepsilon_n}{\varepsilon_{n-1}} \tag{75c}$$

$$\theta_m = \varepsilon_0 \tag{75d}$$

$$\frac{\overline{\langle C_{p,i-1}\rangle}}{\overline{\langle C_{p,i}\rangle}} = \frac{s\varepsilon_{i-1}\tau_i}{\alpha_i^2\Lambda_i(s)} + \frac{1}{\alpha_i} \tag{75e}$$

For an aggregate consisting of one single layer ($n = 1$ and $\varepsilon_1 = 1 - \varepsilon_m$), $M(s)$ reduces to

$$M(s) = \frac{\alpha_1(1 - \varepsilon_m)}{\theta_m} \frac{1}{1 + s\tau_1(1 - \varepsilon_m)} = \frac{K'}{1 + st_M} \tag{76}$$

which is identical to (71) representing the Coats and Smith model. For two layers the expressions for K' and t_M are [*Villermaux*, 1981*a*]:

$$K' = (\alpha_1\varepsilon_1 + \alpha_1\alpha_2\varepsilon_2)/\theta_m \tag{77a}$$

$$t_M = -M'(0)/M(0) = \tau_1(\varepsilon_1 + \alpha_2\varepsilon_2) + \tau_2 \frac{\alpha_2\varepsilon_2^2}{\varepsilon_1 + \varepsilon_2\alpha_2} \tag{77b}$$

A relatively simple expression for K' of the type given by (77*a*) can also be derived for n layers [*Villermaux*, 1981*a*]. Unfortunately, no simple relationship for t_M exists for n layers.

Although attractive in concept the model of layers in series is relatively impractical for two reasons. First, the model involves too many parameters (i.e., α_i, ε_i, τ_i for each layer) which are not easily measured. Second, when α_i, ε_i, τ_i become independent of the index i, the model is a discrete form of the internal diffusion model as can be seen by comparing (74) and (55*a*). Consequently, the models behave similarly when the number of layers becomes greater than 3 or 4. Nevertheless, layers in series can account for a nonuniform distribution of the adsorption capacity (i.e., α_i) or of the diffusion coefficient (i.e., τ_i) inside the aggregate, provided enough experimental data can be obtained to define those distributions.

5.5. *Two Porosity Levels*

The previous model for two layers in series can be refined to account for two porosity levels (Figure 5*b*). This situation is encountered in structured soils when a macroaggregates (or primary ped) is made of microaggregate (or secondary peds) [*Brewer*, 1964; *Hillel*, 1980]. To model this situation, let us first rewrite (43*b*) as

$$L(s) = \frac{\overline{\langle C_p\rangle}}{\overline{C}_e} \tag{78}$$

where C_e is the concentration of the external fluid in contact with the aggregate. For the microaggregate, C_e is the local concentration in the pore fluid of the macroaggregate. Let us assume that mass transfer is controlled by external and internal diffusion, as well as adsorption kinetics. Using (69), (43*a*), (43*b*), (52*a*), and (52*b*), one obtains

$$L(s) = \alpha\left[\frac{1 + A(s)}{H^*(s_3)} + st_e\right]^{-1} \tag{79}$$

Let us use the subscripts *mi* and *ma* to denote variables at the microaggregate and macroaggregate levels, respectively. Knowing that solute concentration in the immobile water phase at the macroporosity level is the external concentration for the microaggregate, the transfer function for the microaggregate is

$$L_{mi}(s) = \frac{\overline{\langle C_{p,mi}\rangle}}{\bar{C}_{im,ma}} = \alpha_{mi}\left[\frac{1 + A_{mi}(s)}{H^*_{mi}(s_3)} + st_{e,mi}\right]^{-1} \tag{80a}$$

$$s_3 = l_{mi}\left\{\frac{s}{D'_{e,mi}[1 + A_{mi}(s)]}\right\}^{1/2} \tag{80b}$$

Using a recurrent method and ignoring adsorption at the macroporosity level, *Authelin* [1988*a*] showed that $L_{ma}(s)$ is given by

$$L_{ma}(s) = \frac{\overline{\langle C_{p,ma}\rangle}}{\bar{C}_m} = \frac{\alpha_{ma}}{st_{e,ma} + \dfrac{1}{H^*_{ma}(s_4)B(s)}} \tag{81a}$$

$$B(s) = \frac{\beta_{ma} + (1 - \beta_{ma})L_{mi}(s)}{\alpha_{ma}} \tag{81b}$$

$$s_4 = l_{ma}\left\{\frac{sB(s)}{D'_{e,ma}}\right\}^{1/2} \tag{81c}$$

$$\alpha_{ma} = \beta_{ma} + (1 - \beta_{ma})\alpha_{mi} \tag{81d}$$

In these equations, β_{ma} is the volume fraction of water in the aggregate macropores relative to the total volume of the macroaggregate, α_{mi} is the equilibrium solute distribution coefficient between the microaggregate and water in the macropores, and α_{ma} is the overall distribution coefficient between the macroaggregate and the mobile water phase. If immobile water is only present in the macropores, then $\beta_{ma} = \beta_{im}$. In (80) and (81) the transfer functions A and H^*, irrespective of the indices, are as defined previously by (66*b*) and Table 1. Notice that the substitution of s_4 for s_2 in H^*_{ma} (equation (81*a*)) is similar to the substitution of s_3 for s_2 made in (68*a*) to account for adsorption kinetics. This means that transfer to the microaggregate can be seen as an adsorption process from the macrolevel and as such forms the basis of the recurrent method for obtaining $L_{ma}(s)$.

Whereas $t_{e,ma}$ is given by (47), $t_{e,mi}$ is different because of the presumed absence of a viscous boundary layer inside the macroaggregate. The parameter $t_{e,mi}$ may be interpreted as the characteristic time of a possible mass transfer resistance at the boundary of the microaggregate. For example, $t_{e,mi}$ could account for noninstantaneous sorption at the surface of a clay crystal before solute penetrates the bulk of the crystal by internal diffusion. Also, the surfaces of microaggregates (or secondary peds) in structured soils are often covered by a variety of constituents (sometimes referred to as ped cutans) such as clay coatings, iron oxides, and organic matter. The physical and chemical properties of these surface coatings can be radically different from those of the soil matrix inside the microaggregates. Excellent discussions of the physical and chemical makeup of structured soils are given by *Brewer* [1964] and *Baver et al.* [1972]. Similar situations also apply to saturated and unsaturated fractured rocks. These examples indicate that appropriate physical and chemical interpretations are necessary in order to express $t_{e,mi}$ in terms of underlying transfer processes and soil properties. They also suggest, as noted before, that a certain characteristic time can have several interpretations depending upon the physical and chemical processes involved, i.e., external diffusion, internal diffusion, kinetic or equilibrium sorption, sorption or diffusion in series, or a combination of some or all of these properties.

Finally, $M(s)$ is obtained by simply inserting L_{ma} in (43*a*). This shows that the process of building and refining $M(s)$ or $L(s)$ can be viewed as the progressive embedding of a limited number of elementary transfer functions in one overall transfer function. As before, (81), (17*a*), and (17*b*) give

$$K' = \alpha_{ma}(1 - \varepsilon_m)/\theta_m \tag{82a}$$

$$t_M = t_{e,ma} + t_{im,ma} + \frac{\alpha_{ma} - \beta_{ma}}{\alpha_{ma}}(t_{e,mi} + t_{im,mi} + t_{\text{des},mi}) \tag{82b}$$

which again shows that the characteristic transfer times are additive. Notice that the last term of (82*b*) acts as the desorption time t_{des} in (70). This means that a desorption time at a macroscopic level can always be interpreted as an equivalent mass transfer time (i.e., $t_{e,mi}$ and $t_{im,mi}$, or even $t_{\text{des},mi}$) at a lower level. In other words, a desorption time is not necessarily the characteristic time of a true chemical adsorption process in the model but rather the characteristic time of a process at a more microscopic scale.

If we approximate $H^*_{ma}(s_4)$ and $H^*_{mi}(s_3)$ by first-order equations which have the same zero and first-order moments, one obtains

$$L_{ma}(s) = \frac{(1 - \beta_{ma})L_{mi}(s) + \beta_{ma}}{1 + s(t_{e,ma} + t_{im,ma})\,\dfrac{(1 - \beta_{ma})L_{mi}(s) + \beta_{ma}}{\alpha_{ma}}} \tag{83a}$$

$$L_{mi}(s) = \frac{\alpha_{mi}}{1 + (t_{e,mi} + t_{im,mi} + t_{\text{des},mi})s} \tag{83b}$$

Finally, we can further reduce $M(s)$ to $N(s)$ by making use of (82*a*) and (82*b*). Note that (83*a*) is the correct form of (24) of *Villermaux* [1987].

5.6. *Discrete Parallel Retention Sites*

This case is encountered when a population of aggregates with different physical or chemical properties is locally in contact with mobile water (Figure 5*c*). There are N aggregate classes, each of which is composed of identical aggregates. A complete model is at present only available in terms of average concentrations $\langle C_{p,i}\rangle$, which are defined as the ratio of the mass of solute in the ith aggregate class to the volume of the entire aggregate population. Let ω_i be the fraction of sorbed solute in the ith aggregate class at equilibrium. Let us further consider mass transfer from mobile water to the ith aggregate class as a first-order process with a mass transfer coefficient k_i. The mass balance equation for the ith aggregate class is

$$V_p \frac{d\langle C_{p,i}\rangle}{dt} = k_i S_{p,i}\left(C_m - \frac{\langle C_{p,i}\rangle}{\alpha_i}\right) \tag{84}$$

where $S_{p,i}$ and $\alpha_i = \alpha\omega_i$ are the external surface area and the distribution coefficient of the ith aggregate class respectively. Applying Laplace transforms and summing over the aggregate population leads to

$$L(s) = \frac{\overline{\langle C_p\rangle}}{\bar{C}_m} = \frac{\sum_{i=1}^{N} \overline{\langle C_{p,i}\rangle}}{\bar{C}_m} = \alpha \sum_{i=1}^{N} \frac{\omega_i}{1 + s\tau_i} \tag{85a}$$

$$\tau_i = \frac{\alpha_i V_p}{k_i S_{p,i}} \tag{85b}$$

The transfer function $M(s)$ for this system is deduced from (43a). A straightforward derivation shows that t_M is given by

$$t_M = \sum_{i=1}^{N} \omega_i \tau_i \tag{86}$$

For a single class of aggregates, $M(s)$ again reduces to $N(s)$. With two classes, (85) enables one to model mass transfer toward equilibrium sites ($\tau_1 \approx 0$, sorption sites in direct contact with mobile water) which are in competition with slowly adsorbing sites ($\tau_2 \gg \tau_1$, sorption sites in contact with immobile water). This situation was considered by *Nkedi-Kizza et al.* [1983].

Depending upon the physical nature of the transfer resistance, different expressions can be derived for τ_i. We only consider here the case where internal diffusion dominates and assume that the soil aggregate population is composed of a discrete set of aggregate size classes. The distribution coefficient $\beta_{im} + \rho_a K_a$ (i.e., α), the shape factor μ, and the bulk density ρ_a are assumed to be identical for all size classes. Consequently, ω_i is the volume or weight fraction of the ith aggregate class. Assuming that the first-order approximation holds for aggregates of any size, and using equation (57), we obtain

$$\tau_i = \mu \frac{l_i^2}{D_e'} \tag{87a}$$

$$t_M = \sum_{i=1}^{N} \mu \frac{l_i^2}{D_e'} \omega_i \tag{87b}$$

$$l_i = \frac{\omega_i V_p}{S_{p,i}} = \frac{V_{p,i}}{S_{p,i}} \tag{87c}$$

where l_i is the ratio of the volume $V_{p,i}$, to the surface area, $S_{p,i}$, of the ith aggregate class.

5.7. *Continuous Distribution of Parallel Retention Sites*

The above model is easily extended to any continuous distribution of parallel retention sites. Let $f(\tau)\, d\tau$ be the fraction of sorbed solute at equilibrium on sites having mass transfer times within τ and $\tau + d\tau$. $L(s)$ is now given by

$$L(s) = \alpha \int_0^{\infty} \frac{f(\tau)\, d\tau}{1 + \tau s} \tag{88}$$

where $f(\tau)$ is referred to as the transfer time distribution (TTD) after *Villermaux* [1973, 1981a, 1987]. Discrete retention sites in parallel are accounted for by a sum of delayed Dirac functions $\delta(\tau - \tau_i)$. From (17b) it follows immediately that

$$t_M = \int_0^{\infty} \tau f(\tau)\, d\tau \tag{89}$$

If we view τ as an internal diffusion time parameter and make the same assumptions as in the previous section, (89) becomes

$$t_M = \mu \frac{\int_0^{\infty} l^2 g_w(l)\, dl}{D_e'} \tag{90}$$

where $g_w(l)$ is the aggregate size distribution by weight. Equation (90) is the continuous formulation of (87b).

We note that when τ is a combination of several characteristic times of the same order of magnitude, the above approach becomes meaningless since the TTD would then depend on several independent and distributed parameters (e.g., l, δ, and k_{des}) instead of a single parameter (e.g., τ).

A TTD can also be approximated by an equivalent first-order transfer function (i.e., $N(s)$ instead of (88)). Such a substitution will always preserve the zero- and first-order moments of $M(s)$. However, we shall show below that such a substitution can be very misleading.

An alternative approach to this problem is given by *Rasmuson* [1985] who focused especially on aggregate size distributions. In another study, *Authelin* [1988a, b] investigated mass transfer to zeolite crystals of distributed size (gas phase experiments). He showed that the TTD approach was necessary to describe the observed BTCs.

5.8. *Effect of First-Order Decay*

In addition to mass transfer and sorption kinetics, solutes may also be subject to chemical reactions during the transport process. To preserve linearity of the problem, we restrict ourselves to first-order kinetics. This case occurs during radioactive decay, certain microbial degradation processes, or when the solute is a reactant at trace levels with respect to other possible coreactants or catalytic sites in the soil. We further assume that the reaction takes place in both the mobile and immobile water phases, and in the adsorbed phase, and that wherever the solute is, it is subject to same first-order decay coefficient k. This situation may not necessarily be correct [*van Genuchten and Wagenet*, 1989].

The transfer function is easily modified for decay by making use of the results from the previous sections. First, note that the net rate of decay, R, of solute in a volume V is given by

$$R = kCV \tag{91}$$

The net rate R' of solute accumulation is

$$R' = V\frac{dC}{dt} \tag{92}$$

The mass balance equation for solute in any given region of the soil (e.g., mobile water, immobile water, adsorbed phase) involves the sum $R + R'$. In the Laplace domain, $R + R'$ becomes

$$\bar{R} + \overline{R'} = V(s + k)\bar{C} \tag{93}$$

which shows that $s + k$ must be substituted for s in $M(s)$ and $G_m(s)$ to account for the first-order decay.

Until now, the mean retention time has been independent of any mass transfer or dispersion process. This situation becomes different when decay takes place. Equation (36) does not hold any more, since the effects of decay were not included in $G_m(s)$. A complete derivation of the mean retention time requires one to go back to (17a) and (17b). Assuming that $M(s) = N(s)$ for the first-order approximation, the transfer function $G_R(s)$ for the decay in a cascade of mixing cells can be readily obtained from (33), (35), and (71) by substituting $s + k$ for s:

$$G_R(s) = G_m\{(s + k)[1 + M(s + k)]\}$$

$$= \left\{1 + \frac{(s + k)t_m}{J}\left[1 + \frac{K'}{1 + (s + k)t_M}\right]\right\}^{-J} \tag{94}$$

Applying (17a) and (17b) to $G_R(s)$ leads to

$$G_R(0) = \left[1 + \frac{t_m}{Jt_R}\left(1 + \frac{K'}{1 + t_M/t_R}\right)\right]^{-J} \tag{95a}$$

$$t_r = t_m\frac{1 + \dfrac{K'}{(1 + t_M/t_R)^2}}{1 + \dfrac{t_m}{Jt_R}\left(1 + \dfrac{K'}{1 + t_M/t_R}\right)} \tag{95b}$$

$$t_R = 1/k \tag{95c}$$

where t_R is a characteristic reaction time. Equation (95b) shows that t_r is affected by kinetic processes as soon as a decay reaction occurs. Comparing t_R, t_m, and t_M allows one to assess the relative importance of the different processes. For example, when t_R is much greater than t_m and t_M, decay may be neglected and (95b) reduces to (36). *Villermaux* [1981b] has given a more detailed approach to account for reversible reactions and different kinetic rate constants depending upon the phase where reactions take place. Using Villermaux's results in the discrete parallel site model of section 5.6 would lead to the two-site transport and degradation model of *van Genuchten and Wagenet* [1989].

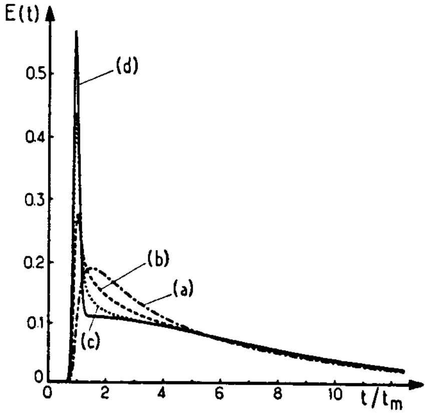

Fig. 6. Effects of internal and external mass transfer kinetics on calculated breakthrough curves for a weakly dispersive system, assuming spherical aggregates, $J = 100$ ($P = 200$, $t_D/t_m = 5\ 10^{-3}$), $K' = 5$, and $t_M/t_m = 2.4$ for all curves. Curve a was obtained with $t_{im}/t_m = 1.8$, $t_e/t_m = 0.6$, curve b with $t_{im}/t_m = 1.2$, $t_e/t_m = 1.2$, curve c with $t_{im}/t_m = 0.6$, $t_e/t_m = 1.8$, and curve d with $t_{im}/t_m = 0$, $t_e/t_m = 2.4$. Figure 6d represents the first-order approximation.

5.9. *A Comparison of the Transfer Function Models*

To conclude this section, we present some simulation results to assess the validity and limitations of first-order approximations given by (58), (83a), or (83b) and to study the properties of sites in parallel. As in section 3, we consider the example of one-dimensional convective-dispersive transport in a single porosity soil system with equilibrium sorption. The residence time distribution for the mobile water phase $E_m(t)$ is then given by the mixing cell in series model. For a single retention site the transfer function for the detailed model with internal diffusion is

$$G_{\text{det}}(s) = \left\{1 + \frac{st_m}{J}\left[1 + \frac{K'}{\dfrac{1}{H(s)} + st_e}\right]\right\}^{-J} \tag{96}$$

With the first-order approximation (71) a simplified transfer function is obtained

$$G_{\text{sim}}(s) = \left[1 + \frac{st_m}{J}\left(1 + \frac{K'}{1 + st_M}\right)\right]^{-J} \tag{97}$$

where t_M is given by the sum of the characteristic mass transfer times (equation (70)). Note that the simplified transfer function is obtained by setting $t_{im} = 0$ and $t_e = t_M$ in the detailed model.

Figures 6 and 7 illustrate the effects of external and internal mass transfer kinetics on BTCs obtained in a weakly dispersive system (i.e., $t'_M \gg t_D$). The aggregates are assumed to be spherical. In Figure 6, $t_M/t_m = 2.4$ for all cases, leading to BTCs which are quite asymmetrical since $t_M \gg t_m$ (compare with Figure 3). When external mass transfer dominates (Figures 6c and 6d), there is a sharp leading peak located around $t = t_m$. On the other hand, when internal diffusion is dominant (Figure 6a), the sharp peak disappears and the simplified model (Figure 6d) becomes questionable. In Figure 7, $t_M/t_m = 0.6$, causing all BTCs to become more symmetrical than in Figure 6. Irrespective of the contributions of external and internal mass transfer, the BTCs are almost identical which shows that the simplified model is now a good approximation. We conclude that the simplified model, i.e., $G_{\text{sim}}(s)$, will yield accurate results in most situations, except when $t_{im} \gg t_e$ and $t_M \gg t_m$. If experiments are performed under conditions where

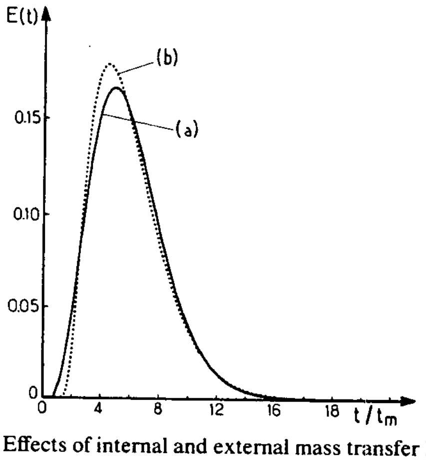

Fig. 7. Effects of internal and external mass transfer kinetics on calculated breakthrough curves for a weakly dispersive system with $J = 100$ ($P = 200$, $t_D/t_m = 5\ 10^{-3}$), $K' = 5$, and $t_M/t_m = 0.6$ for all curves. Curve a was obtained with $t_{im}/t_m = 0.6$, $t_e/t_m = 0$, and curve b with $t_{im}/t_m = 0$, $t_e/t_m = 0.6$. Curve b also represents the first-order approximation.

the simplification holds, discrimination among the different models and the contributions to t_M will be extremely difficult if not meaningless.

Figure 8 compares the simplified model (first-order approximation) with the detailed model in the absence of external mass transfer limitations, assuming that the aggregate is either a sphere or a slab. Result show that the aggregate shape is of little importance in the detailed model. Here again, the first-order approximation does not hold because $t_M = t_{im} \gg t_m$.

Figure 9 illustrates the effect of different transfer time distributions (TTDs) for identical t_m, K', J, and t_M on calculated BTCs. In other words, the mean retention time and variance of all BTCs are independent of the TTD (see equation (90)). The figure shows that different TTDs with the same mean time t_M can lead to different BTCs. This means that the variance of the TTD is a crucial parameter affecting the shape of a BTC. To our knowledge, only the TTD is ultimately responsible for the very different shapes of BTCs having the same mean and variance. Classical models excluding TTD will always give similar BTCs as soon as the means and variances are matched, especially when t_M is smaller than t_m (Figure 7). This is due to the fact that $M(s)$ is well approximated by the first-order function $N(s)$ in these models, whereas $M(s)$ as defined by (88) is not (except again when $f(\tau)$ reduces to a single delayed Dirac δ function). This point will be discussed in detail in section 7.

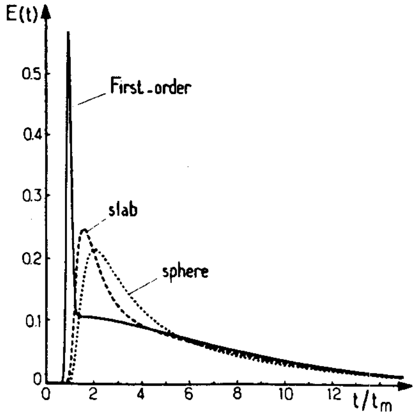

Fig. 8. Comparison of calculated breakthrough curves showing the effects of aggregate shape, and first-order approximation for predominantly internal diffusion ($J = 100$, $K' = 5$, $t_{im}/t_m = 2.4$).

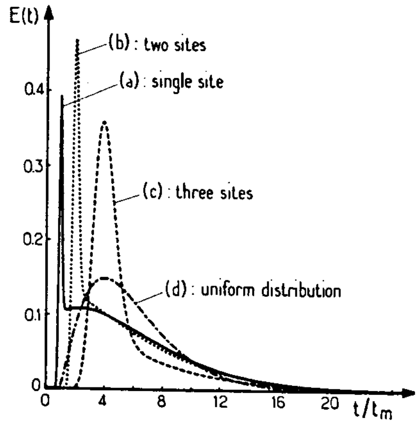

Fig. 9. Effects of different transfer time distributions on calculated breakthrough curves assuming $J = 100$, $K' = 5$, and $t_M/t_m = 2$. Curve a is for a single site with $\tau/t_m = 2$; curve b is for two sites with $\omega_1 = 0.2$, $\tau_1/t_m = 0$, $\omega_2 = 0.8$, and $\tau_2/t_m = 2.5$; curve c is for three sites with $\omega_1 = 0.2$, $\tau_1/t_m = 0$, $\omega_2 = 0.4$, $\tau_2/t_m = 1$, $\omega_3 = 0.4$, and $\tau_3/t_m = 4$, and curve d is for a uniform distribution varying from $\tau/t_m = 0$ to $\tau/t_m = 4$. All transfer time distributions have the same mean time $t_M = 2t_m$.

When no TTD is involved, asymmetrical BTCs have their maximum located close to $t = t_m$ (see Figure 3 with $t'_M/t_m = 0.44$ and Figures 6a–6d and 8). When a TTD is involved, Figures 9b–9d show that the maximum can be delayed with respect to t_m. This property indicates that a TTD involving a fast exchanging site is necessary to account for the observed BTC.

6. SIMULATING $G_m(s)$ WITH A CELL NETWORK MODEL

In addition to needing a model, $M(s)$, for transfer at the local level a second model is necessary for $G_m(s)$, the Laplace transform of the RTD of the solute in the mobile water phase (section 4). We again assume steady flow and show that system dynamics is a powerful tool for generalizing the mixing cell in series model. Moreover, we will give a description for mobile water transport in more general terms than only the RTD, $E_m(t)$.

The porous medium is assumed to be a one-dimensional or multidimensional network of mixing cells [*Rao and Hathaway*, 1989] as shown in Figure 10. Each cell, j, has a total volume V_{Tj}, a mobile water content θ_{mj}, and a volume of mobile water $V_j = \theta_{mj} V_{Tj}$. The volumetric flow rate from cell i to cell j is denoted by q_{ij}. We assume that the indices i and j are properly ordered and that $q_{ii} = 0$. Since we are modeling convective transport in the mobile water phase only, the mass balance equation for cell j is

$$\frac{dC_{mj}}{dt} = \frac{1}{V_j}\left(\sum_{i=1}^{J} q_{ij}C_{mi} + q_{Ej}C_{mEj} + q_{Ij}C_{mIj} - Q_jC_{mj}\right) \tag{98}$$

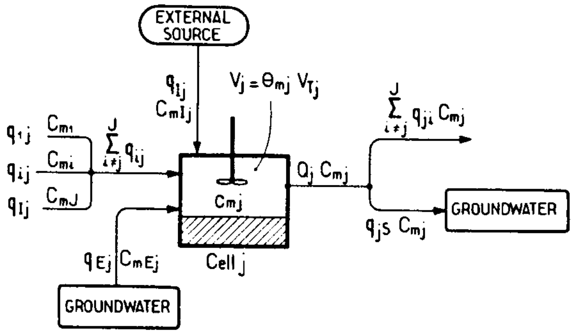

Fig. 10. Schematic of a cell environment in a flow network.

where q_{Ij} and q_{Ej} are flow rates coming from an external source (artificial injection in cell j) and from the natural groundwater environment, respectively. C_{mIj} and C_{mEj} are the respective solute concentrations in these two fluxes. We assume that C_{mEj} is time independent, at least for the duration of an experiment. The total flow rate Q_j through cell j is defined by

$$Q_j = q_{Ej} + q_{Ij} + \sum_{i=1}^{J} q_{ij} \tag{99}$$

The flow rate q_{jS}, leaving cell j toward the groundwater environment or an external sink, is

$$q_{jS} = Q_j - \sum_{i=1}^{J} q_{ji} \tag{100}$$

Let $C_{j,ss}$, $C_{Ej,ss} = C_{Ej}$, $C_{Ij,ss}$ be the concentrations at steady state. Equation (98) gives

$$\sum_{i=1}^{J} q_{ij}C_{i,ss} + q_{Ej}C_{Ej,ss} + q_{Ij}C_{Ij,ss} - Q_jC_{j,ss} = 0 \tag{101}$$

Subtracting (101) from (98) gives

$$\frac{dC'_{mj}}{dt} = \frac{1}{V_j}\left(q_{Ij}C'_{mIj} - Q_jC'_{mj} + \sum_{i=1}^{J} q_{ij}C'_{mi}\right) \tag{102}$$

where C'_m are concentration deviations from the steady state values. Equation (102) is identical to (98) except that external solute fluxes from the environment have been canceled. This shows that constant fluxes from the environment can always be canceled by appropriately shifting the zero concentration level of each cell. Below we will use (102) without primes on the concentration variables. In the Laplace domain, (102) reduces to

$$(1 + st_{mj})\bar{C}_{mj} = \frac{q_{Ij}}{Q_j}\bar{C}_{mIj} + \sum_{i=1}^{J} \frac{q_{ij}}{Q_j}\bar{C}_{mi} \tag{103}$$

where $t_{mj} = V_j/Q_j$ is the mean convection time of mobile water in cell j. Using matrix notation, (103) may be written in the form

$$[\Gamma(s)]_{J,J}[\bar{C}_m]_{J,1} = [\bar{Y}]_{J,1} \tag{104}$$

where $[X]_{p,q}$ is a matrix with p rows and q columns. A comparison of (103) and (104) gives the elements of $[\Gamma]$ and $[\bar{Y}]$,

$$\begin{aligned} \Gamma_{ij}(s) &= -q_{ij}/Q_j \qquad i \neq j \\ \Gamma_{ij}(s) &= 1 + st_{mj} \qquad i = j \end{aligned} \tag{105}$$

$$\bar{Y}_j = \frac{\bar{C}_{mIj}q_{Ij}}{Q_j} \tag{106}$$

The concentration response of any cell to an arbitrary injection vector $[\bar{Y}]$ is thus given by

$$[\overline{C_m}]_{J,1} = [\Gamma(s)]^{-1}_{J,J}[\bar{Y}]_{J,1} \tag{107}$$

where $[\Gamma(s)]^{-1}_{J,J}$ is the inverse of a transfer matrix generalizing the transfer function concept. When $q_{Ii}\bar{C}_{mIi} = 1$ and $\bar{C}_{mIk} = 0$ $(k \neq i)$, $q_{jS}\bar{C}_{mj}$ is the flux response of cell j to a Dirac input of nonreactive solute in cell i. In general, this is not the RTD as defined in section 2.2. It is a RTD when q_{Ii} and q_{jS} are the only fluxes between the environment and the cell network. This situation represents an isolated streamtube with only one inlet and one outlet. When there are several inlet and outlet fluxes toward the environment, $\bar{C}_{mj}$ defines a partial RTD upon normalization. Presently, the properties of these partial RTDs have not been investigated in detail, even in chemical engineering.

If we want the overall system response in the presence of solute transfer, (33) shows that $s[1 + M(s)]$ should be substituted for s in (107). If necessary, different transfer functions $M_j(s)$ can be inserted in the expressions for $\Gamma_{jj}(s)$ (equation 105)) to account for different physicochemical properties of the different mixing cells. This approach allows us to relax the assumption that all mass transfer coefficients and sorption capacities must be independent of the location in the soil system as it has been assumed by *Villermaux* [1973] when he demonstrated the uncoupling relationship (33).

The above theoretical approach permits the description of many situations when networks are chosen in accordance with the prevailing soil structures or of the shape of the observed partial RTD. For instance, a soil consisting of two layers with different hydraulic properties, or a partial RTD exhibiting two successive maxima, can be modeled by two parallel series of mixing cells, thus characterizing two parallel convective-dispersive flows.

7. DISCUSSION AND CONCLUSIONS

We have shown that system dynamics and the concept of residence time distribution are powerful tools for modeling the transport of linearly interacting solutes. The method consists of first modeling the process at the smaller local level and then progressively incorporating transfer functions of various sublevels into the transfer function of an immediately higher level. The uncoupling theorem (equation (33)) is an illustration of this method which enables one to separately study solute transfer to a stationary phase and solute transport in mobile water. The intermediate variables s_3 and s_4 illustrate the incorporation of adsorption kinetics in $H(s)$ and the incorporation of the microaggregate dynamics in the macroaggregate transfer function, respectively.

Solute transfer is described by a transfer function $M(s)$, which involves two types of parameters: distribution coefficients, α, and characteristic kinetic times, t with various indices. First, we note that all characteristic times incorporate distribution coefficients reflecting equilibrium properties of the soil system. This suggests that any interpretation or estimation of a kinetic parameter requires an accurate description of the equilibrium properties. Second, the characteristic times can have different physical interpretations, although their occurrence in $M(s)$ needs to be established only once. This problem is illustrated by the possibility of having different interpretations for a desorption time at the macrolevel in terms of mass transfer times at the microlevel, by different assumptions about diffusion of adsorbed solutes, or by different interpretations of $t_{e,ma}$ and $t_{e,mi}$. Thus the few generalized transfer functions described in this paper can cover a large number of conceptually different physical and chemical situations. This is the principle of system dynamics which enables one to describe transient processes more or less independently of possible physical interpretations.

Unfortunately, the possibility of having multiple interpretations of the transport process also suggests that solving the inverse problem to recover the basic physical mechanisms from a BTC is an inherently ill-posed problem. Except for retention sites in parallel, all models for $M(s)$ are represented accurately by the first-order approximation, $N(s)$. This means that several models can yield the same good fit of an experimental BTC, and hence will result in the same value of the overall characteristic time t_M. Consequently, the question arises of how to interpret an experimental BTC if the theoretical curve is relatively insensitive to model structure?

One possible approach may be to first analyze the physical meaning of the most reliable parameters such as the overall characteristic time t_M. For instance, if t_M is found to be independent of the aggregate size l, the dominant process is probably desorption (equation 65)). On the other hand, when t_M depends on the square of l, internal diffusion (equation (57)) should be the dominant process. Unfortunately, it is not easy to vary l in soil systems.

Another and more original approach would be to take advantage of the relative insensitivity of BTCs to model structure. When a detailed model is fitted to an experimental BTC the resulting parameters are likely quite unreliable. However, if the curve fit is good, the model is at least able to accurately reproduce the BTC and hence also its time moments. The possibly unreliable parameters can then still be used to accurately calculate numerical values for the time moments of any order and, for instance, the reduced variance. The different theoretical expressions for the variance, depending upon the physical interpretations, could suggest which operating or physical variables could be varied to test the interpretation against new experiments. *Authelin et al.* [1988*a*, *b*] showed that this method can lead more accurate variances, especially in comparison to direct calculation from the experimental curves using (9) or (11). In a second step, these authors used the accurate numerical variance to investigate diffusion in a zeolite-based catalyst with two porosity levels. The procedure was called the "moment fitting method."

A third possible approach would be to estimate some of the characteristic times on the basis of physical and structural data in order to reduce the number of independent fitting parameters. For instance, the thickness of the viscous boundary layer is easily estimated from chemical engineering correlations [*Froment and Bischoff*, 1979; *Levenspiel*, 1972; *Villermaux*, 1982]. In some cases, studies have claimed that these a priori estimates do not work very well. A likely reason for this failure is that the estimated parameters often have no relevance to the processes being studied. *Hutzler et al.* [1986], *Crittenden et al.* [1986], *Roberts et al.* [1987], *Nicoud and Schweich* [1989], and *Brusseau et al.* [1989] have shown that independent estimates can be quite reliable, provided that the physical processes responsible for the observed BTCs are well understood.

Whatever approach is followed, fitting of kinetic parameters to BTCs can at most be indicative of the most relevant underlying mass transfer processes. Validation of the interpretation can only be made by suitable experimental procedures (not only breakthrough experiments) which must be tailored to the assumed mass transfer process. The obvious consequence is that understanding the underlying processes is more a problem of physics and chemistry than one of curve fitting.

Another question is what to do when the classical models are unable to reproduce the experimental BTCs or when proper interpretation of t_M seems impossible or questionable? This question is implicitly raised by *Hutzler et al.* [1986] who studied mass transfer in a laboratory column packed with soil particles with sizes ranging from 0.05 to about 0.5 mm. On the basis of least squares fitting of the observed BTCs they concluded that internal diffusion was the controlling mass transfer process. The aggregate size was considered as the single unknown parameter in the fitting procedure. They observed that the best descriptions were obtained with an aggregate size which was about 10 times larger than the mean particle size. The aggregate size was also found to vary with solute and pore water velocity. Although "aggregate" is an ill-defined entity, these and other anomalous results can be explained readily by the TTD concept. First, note that a tenfold range in the particle-size distribution results in a 100-fold range in the associated internal mass transfer times (equation (57)). As was shown in Figure 9, different TTDs with the same mean t_M can lead to radically different BTCs. Consequently, when the transfer function $M(s)$ of a relatively broad TTD (equation (88)) is approximated by a first-order model, $N(s)$, the results can become very misleading even though the fit seems good. Moreover, (90) shows that the mean mass transfer time t_M of an equivalent single adsorption site depends on the second order moment of the aggregate size distribution by weight. For a broad distribution the second-order moment can be much larger than the square of the first-order moment. This property could potentially explain the large value of the fitted aggregate size found by Hutzler et al.

The variation of the mean aggregate size with pore water velocity and the injected solute tracer as reported by *Hutzler et al.* [1986] can also be explained by the TTD concept. Assuming that $\sigma_m'^2 = 2/P$ and using (39*a*), (39*b*), and (86), one obtains

$$\sigma'^2 = \frac{2}{t_m}\left(t_D + \frac{K'}{(1+K')^2}\sum_{i=1}^{N}\omega_i\tau_i\right) \qquad (108)$$

Let us use the term "fast site subpopulation" (FSSP) for the largest set of sites k which satisfies

$$\sum_{k}\omega_k\tau_k \le \frac{(1+K')^2}{K'}t_D \qquad (109)$$

in which τ_k can be either a transfer time which is much smaller than t_D or a larger transfer time of small weight ω_k. As illustrated in Figure 3, BTCs are affected by internal mass transfer when the contribution of this mass transfer process to the overall variance is larger than the contribution of the dispersion process ($t'_M > t_D$). Equation (109) suggests that sites of the FSSP do not significantly affect BTCs. Consequently, least squares fitting of a BTC will ignore these sites and results in an apparent mean transfer time t''_M given by

$$t''_M = \sum_{i \notin \text{FSSP}} \omega_i \tau_i \qquad (110)$$

Although τ_i is assumed to be independent of the pore water velocity, t_D should in general depend on the flow rate. Hence the FSSP and t''_M should also depend on flow rate. Finally, (109) indicates that the FSSP and t''_M depend on the solute tracer through K'. Consequently, when t''_M is interpreted in terms of the apparent aggregate size, the fitted size will depend on the pore water velocity and the injected solute as well. From a qualitative point of view, all observations reported by Hutzler et al. can be explained with the above FSSP and the fact that these authors used an equivalent first-order system to account for a broad transfer time distribution. Notice however, that other explanations are possible. For instance, *Cui et al.* [1990] showed that a flow rate dependent mass transfer time can be due to a radially non uniform fluid velocity.

Even if the model for $M(s)$ is fundamentally sound, one still must determine $G_m(s)$. Although the uncoupling theorem provides a basis of our modeling method, (33) is merely a theoretical relationship which eventually defines $G_m(s)$. Since any solute is transferred to immobile water, $E_m(t)$ cannot be measured. $E_m(t)$ can only be approximated using solutes for which $M(s)$ is presumably known. Consequently, a good model for $E_m(t)$ should result more from a proper physical understanding of the flow structure, than from the inclusion of many fitting parameters. We strongly emphasize that determining kinetic parameters by least squares curve fitting on experimental BTCs requires an accurate model for $E_m(t)$ [*Cui et al.*, 1990].

As a general conclusion, we believe little is gained by using overly sophisticated transport models without a concomitant understanding of the fundamental physical and chemical processes involved. Working with transport models as such adds little to our understanding of the assumed processes. On the other hand, the interpretation of model parameters, and a study of their sensitivity to selected physical, chemical, and other parameters adds much more to our understanding of underlying transport processes. We also believe that the TTD concept should be recommended for modeling soil systems with distributed properties such as aggregate size, or fracture width in fractured media. However, the distribution must be determined independently of any fit to observed BTCs. Although our conclusions are drawn from transport studies involving linearly interacting solutes, they apply equally well or more to nonlinear sorption. In the latter case, BTCs broadening is not only due to dispersion and various kinetic processes but also to nonlinear equilibrium sorption. Evaluation of the contributions to transport of these three often simultaneous processes remains an overwhelming challenge in soil science and hydrology and even chemical engineering.

APPENDIX

Consider a linear dynamic system relating $x(t)$ and $y(t)$. The transfer function is

$$G(s) = \frac{\bar{y}(s)}{\bar{x}(s)} \qquad (A1)$$

Using the Laplace transform theory, it can be shown that

$$\lim_{s \to 0} s\bar{y}(s) = \lim_{t \to \infty} y(t) = y(\infty) \qquad (A2)$$

Assume that $x(t)$ is a step change given by

$$x(t) = aH(t), \qquad \bar{x}(s) = \frac{a}{s} \qquad (A3)$$

Combining (A1), (A2), and (A3) gives

$$G(0) = \frac{y(\infty)}{a} = \frac{y(\infty)}{x(\infty)} \qquad (A4)$$

where $y(\infty)$ and $x(\infty)$ are constant since a linear system asymptotically reaches a steady state upon a step change of the input. Moreover, any steady state can be considered as the asymptotic state of an earlier step change. Consequently, (A4) shows that $G(0)$ is the ratio y/x at steady state in the real time domain.

NOTATION

Definition or first use of a symbol is indicated between parentheses.

$A(s)$	adsorption transfer function (equation (66*b*)).
$B(s)$	transfer function coupling macropores and micropores (equation (81*b*)).
$C(t)$, $C(L, t)$, $C(0, t)$	concentration signals $[ML^{-3}]$.
C_e	concentration of solute in contact with an aggregate $[ML^{-3}]$ (equation (78)).
C_m, $C_{m,s}$	concentration of solute in mobile water, at aggregate boundary (M of solute/L^3 of mobile water) (equations (19) and (45)).
C_{im}	concentration in immobile water (M of solute/L^3 of immobile water) (equation (19)).
C_p	concentration of solute in an aggregate (M of solute/L^3 of aggregate) (equation (40)).
D_e	effective internal diffusion coefficient $[L^2T^{-1}]$ (equation (54)).
D'_e	apparent effective internal diffusion coefficient $[L^2T^{-1}]$ (equation (55), (59), (61), and (62)).
D_{es}	effective surface diffusion coefficient $[L^2T^{-1}]$ (equation (60)).
D	longitudinal dispersion $[L^2T^{-1}]$

	(equation (19)).
D_{mol}	ionic or molecular diffusion coefficient in free water $[L^2T^{-1}]$ (equation (44) and (54)).
$E(t_s)$	residence time distribution (RTD) $[T^{-1}]$ (equation (4)).
$E_m(t)$	residence time distribution of mobile water $[T^{-1}]$.
$E_{m,ij}(t)$	partial residence time distribution from cell i to cell $j[T^{-1}]$.
$F(t_s)$	cumulative residence time distribution (equation (7)).
$f(\tau)$	transfer time distribution $[T^{-1}]$ (equation (88)).
$G(L, s)$, $G(s)$, $G_j(s)$	transfer functions excluding chemical reaction decay.
$G_m(s)$	transfer function of a nonreactive solute in the mobile phase (equations (33a) and (35)).
$G_R(s)$	transfer function including chemical reaction decay (equation (94)).
$g_w(l)$	aggregate size distribution by weight $[L^{-1}]$ (equation (90)).
H	height of the bundle of tubes.
$H(s)$	transfer function accounting for internal diffusion (equation (49)).
$H(t)$	Heaviside function.
J	number of mixing cells.
K'	capacity factor (equations (36) and (52)).
K_a	adsorption constant (L^3 of liquid/M of solid) (equation (41)).
K_{im}	θ_{im}/θ_m (equation (22)).
k	rate constant of a first-order chemical reaction $[T^{-1}]$ (equation (91)).
k_{des}	desorption rate constant $[T^{-1}]$ (equation (63)).
k_e	external mass transfer coefficient $[LT^{-1}]$ (equation (44)).
k_i	mass transfer coefficient for site i $[LT^{-1}]$ (equations (73) and (84)).
k_M	overall mass transfer coefficient $[T^{-1}]$ (equation (20) and (27)).
L	length $[L]$.
L_s	length of a tube $[L]$.
$L(s)$	transfer function for the mass transfer process relating solute concentrations (equation (43b)).
l	characteristic length of an aggregate $(V_p/S_p)[L]$ (equation (46)).
$M(s)$	transfer function for the mass transfer process relating solute amounts (equations (22), (33b), (34), and (43a)).
$N(s)$	first-order approximation for $M(s)$ (equation (71)).
n_0	amount of tracer injected $[M]$.
n_{im}, n_m, n_a	amount of solute in immobile, mobile water, adsorbed $[M]$.
P	Péclet number (equation (25)).
Q	volumetric flow rate $[L^3T^{-1}]$.
Q_j	total flow rate through cell j $[L^3T^{-1}]$ (equation (99)).
q_{Ej}	volumetric flow rate from groundwater to cell j $[L^3T^{-1}]$ (equation (98)).
q_{ij}	volumetric flow rate from cell i to cell j $[L^3T^{-1}]$ (equation (98)).
q_{Ij}	volumetric flow rate of injection to cell j $[L^3T^{-1}]$ (equation 98)).
q_{jS}	volumetric flow rate from cell j to environment or outlet piezometer $[L^3T^{-1}]$ (equation (100)).
q_s	specific flux $[ML^{-2}T^{-1}]$ (equations (44) and (53)).
R	net rate of reaction $[MT^{-1}]$ (equation (91)).
R'	net rate of accumulation $[MT^{-1}]$ (equation (92)).
S	concentration of adsorbed solute (M of solute/M of solid).
s	Laplace parameter $[T^{-1}]$.
s_1, s_2, s_3, s_4	modified Laplace parameters (equations (33b), (56a), (68b), and (81c)).
S_p	external surface area of an aggregate $[L^2]$ (equation (45)).
t	time $[T]$.
t_D	characteristic dispersion time $[T]$ (equations (32a) and (32b)).
t_{des}	characteristic desorption time $[T]$ (equation (65)).
t_e	characteristic external mass transfer time $[T]$ (equation (47)).
t_{im}	characteristic internal diffusion time $[T]$ (equation (57)).
t_M	overall characteristic transfer time $[T]$ (equations (38)).
t'_M	modified overall characteristic transfer time $[T]$ (equations (31b) and (39c)).
t''_M	apparent overall characteristic transfer time $[T]$ (equations (109)).
t_m	characteristic convection time in mobile water $[T]$ (equations (25b)).
t_R	characteristic reaction time $[T]$ (equation (95c)).
t_r	mean retention time $[T]$ (equations (36) and (95b)).
t_s	residence time $[T]$.
$\bar{t}_s$	mean residence time $[T]$ (equations (10), (13), and (15)).
$\bar{t}(0)$	mean time of the input signal $[T]$ (equation (18a)).
$\bar{t}(L)$	mean time of the output signal $[T]$ (equation (18a)).
v	pore water velocity $[LT^{-1}]$ (equation (19)).
u	fluid velocity in the bundle of parallel tube model.

V	total volume $[L^3]$.
Vj	volume of mobile water in cell $j[L^3]$ (equation (98)).
V_a	volume accessible to the fluid $[L^3]$ (equation (15)).
V_p	volume of an aggregate $[L^3]$ (equation (45)).
V_{Tj}	total volume of cell $j[L^3]$.
x	abscissa $[L]$.
Y	defined by equation (106).
$y(t)$, $y(L, t)$, $y(0, t)$	concentration signal $[ML^{-3}]$.

Greek symbols

α	distribution coefficient (equation (41)).
β_{im}	volume fraction of immobile water relative to aggregate volume (equation (40)).
δ	viscous boundary layer thickness $[L]$ (equation (44)).
$1 - \varepsilon_m$	volume fraction of aggregates relative to the whole volume (equation (43*a*)).
ε_i	volume fraction of layer i relative to aggregate volume (equation (75)).
$\Gamma(s)$	defined by equation (104).
θ_m, θ_{im}	volume fraction of mobile and immobile water relative to the whole volume.
Λ_i	transfer function defined by equation (75*b*).
μ	shape factor (equation (57)).
μ_k	kth-order time moment of the RTD $[T^k]$ (equation (9)).
μ'_k	kth-order time moment of the RTD centered about the mean $[T^k]$ (equation (11)).
ρ_a	bulk density of aggregates $[ML^{-3}]$.
σ^2	variance of the RTD $[T^2]$ (equation (12*a*) and (14)).
σ'^2	reduced variance (equation (12*b*)).
σ'^2_m	variance of $E_m(t)$ reduced by t_r^2 (equation (37)).
σ'^2_{im}	mass transfer contribution to the reduced variance (equation (39*b*)).
$\sigma^2(0)$	variance of the input signal $[T^2]$ (equation (18*b*)).
$\sigma^2(L)$	variance of the output signal $[T^2]$ (equation (18*b*)).
τ	tortuosity factor (equation (54)).
τ_i	characteristic transfer time for layer or site $i[T]$ (equations (73) and (85*b*)).
Ω	cross-section area $[L^2]$.
ω_i	fraction of solute in ith aggregate at equilibrium (equation (85*a*)).

Subscripts

des	desorption.
det	detailed.
E	environmental groundwater.
I	injection.
i,k	layer of retention site i, k.
im	immobile water.
j	cell j.
m	mobile water.
ma	macropores.
mi	micropores.
p	total on the aggregate.
s	at aggregate boundary.
ss	steady state.
sim	simplified.

Superscripts

x^+	just downstream location x.

Other

$\bar{f}(s)$	Laplace transform of $f(t)$ (equation (1)).
$\langle X \rangle$	averaged value of X over aggregate volume.
∇	gradient operator.
$[A]$	matrix A.

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