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Dr. Malcolm D. Siegel *WM-RES*
 Division 6431 *WM Record File*
 Sandia National Laboratories *A1756*
 Albuquerque, NM 87185 *SNL*

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Dear Dr. Siegel:

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SUBJECT: CONTRACT NO. *NRG-50-19-03-01/FIN A-1756*, "GEOCHEMICAL SENSITIVITY ANALYSIS"
 (Return to WM, 623-SS) *ch*

I have reviewed the August, 1985 monthly progress report for the above contract, dated September 13, 1985. Based on my review of this report, progress to date is satisfactory. We discussed most of the material in the report during my visit to Sandia on September 9-11, and I have no additional comments on the material in the report at this time.

Please prepare a trip report for the coupled processes symposium held at LBL on September 18-20, 1985. Enclosed please find the final version of the EPA HLW Standards and an article which may be of interest.

The action taken by this letter is considered to be within the scope of the current contract FIN A-1756. No changes to costs or delivery of contract products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contracted products.

Sincerely,

Walton R. Kelly
 Geochemistry Section
 Geotechnical Branch
 Division of Waste Management
 Office of Nuclear Material Safety
 and Safeguards

Enclosure:
As Stated

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Validity of the Local Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils

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Sorption processes that occur during reactive solute movement through porous media can be modeled using either an equilibrium or kinetic approach. Because of the resulting conceptual and mathematical simplification, many transport models assume local chemical equilibrium is valid for describing sorption reactions. This paper presents quantitative criteria to assess the validity of the local equilibrium assumption for one-dimensional, steady flow through homogeneous soils. A method is described whereby formulas for solute breakthrough curve time moments can be determined without knowledge of the analytical solution to the mass transport model. This method is applied to several commonly used nonequilibrium formulations as well as the standard linear equilibrium model. The formulations considered include both the physical nonequilibrium models where the sorption rate is controlled by diffusive solute transfer between mobile and stagnant fluid zones and the chemical nonequilibrium models where the overall sorption rate is governed by the rate of reaction at the soil-solution interfaces. Criteria for local equilibrium to be valid are derived by comparing the time moment formulas for the nonequilibrium and equilibrium models. These criteria explicitly show that basic system parameters (e.g., seepage velocity, dispersion coefficient, distribution coefficient, sorption rate, boundary conditions) have a significant influence on the attainment of local equilibrium.

INTRODUCTION

Adsorption reactions are important processes governing the fate of dissolved hazardous substances in groundwater. Models of the transport of such substances must therefore incorporate mathematical descriptions of the chemical process of adsorption as well as the physical processes of advection and dispersion. On a microscopic level, sorption reactions are complex, time-dependent phenomena involving transport from the bulk aquifer pore fluid to the soil-solution interfaces where sorption occurs. As was noted recently by Rubin [1983], an accurate representation of sorption kinetics requires quantitative treatment of the microscopic transport steps which thus necessitates the specification of the geometry of the sorbent material. For naturally occurring porous media, accurate knowledge of this level of microscopic detail is impossible; however, if the microscopic processes are "fast enough" with respect to the bulk fluid flow rate, then reversible sorption reactions can be assumed to be in a state of local chemical equilibrium. In this paper, such an assumption will be referred to as local equilibrium assumption (LEA).

The LEA results in significant conceptual as well as mathematical simplification; description of the microscopic reaction pathways becomes unnecessary, and the appropriate chemical equations are algebraic formulas (e.g., Freundlich, Langmuir isotherms) whose parameters can be measured by simple batch laboratory experiments. Thus it is not surprising that many investigations to date have invoked the local equilibrium assumption. However, as is evident from the partial list of laboratory column experiments given in Table 1, models based upon LEA do not always accurately simulate sorbing solute transport. If local equilibrium is not attained, LEA-based models will predict a breakthrough response that occurs too late and exhibits too little dispersion. For hazardous solutes, such miscalculations could have grave consequences.

Considering the large number of transport models that have been formulated utilizing either equilibrium or kinetic reaction

submodels, it is surprising that there have been so few investigations into the conditions under which LEA breaks down. In an interesting study, James and Rubin [1979] performed laboratory column experiments over a range of seepage velocities and found that the equilibrium theory failed at the higher fluxes (see Table 1). By using the model of Glueckauf [1955], James and Rubin concluded that the local equilibrium assumption applies when the ratio of the hydrodynamic dispersion coefficient to the molecular diffusion coefficient is "near unity." However, Table 1 does indicate several investigations where equilibrium models proved successful under conditions where hydrodynamic dispersion was significantly greater than molecular diffusion (10^{-6} cm²/s is a typical value of molecular diffusivity). Bolt [1979] studied the criterion for LEA validity by performing a theoretical analysis of solute movement through an aggregated soil; however, his analysis neglected the effect of hydrodynamic dispersion. Palciauskas and Domenico [1976] studied only steady state conditions in their theoretical examination of diffusion-controlled carbonate dissolution. More recently, Jennings and Kirkner [1984] performed a numerical simulation of one-dimensional multispecies transport governed by a kinetic form of the competitive Langmuir isotherm. By repeatedly executing the simulation model under a variety of conditions, they were able to identify ranges of parameter values for which the computed concentration profiles were indistinguishable from those generated by a LEA-based model. In a recent review article, Rao and Jessup [1983] present several commonly utilized nonequilibrium transport models, and they discuss the significance of nonequilibrium indices which arise when the transport equations are nondimensionalized. In the work here we will show that the validity of LEA depends upon several parameters in addition to Rao and Jessup's nonequilibrium indices.

The purpose of this paper is to elucidate the conditions for which local equilibrium is a valid assumption for modeling the transport of sorbing solutes through homogeneous soils. In order to accomplish this objective we consider three commonly used models of sorbing solute transport through a one-dimensional, homogeneous soil column. In two of the models the sorption rate is controlled by diffusive solute transfer be-

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TABLE 1. Review of Experimental Studies of Solute Transport in Saturated Soil Columns

Reference	Porous Medium	Solute	Seepage Velocity, cm/s	Dispersion Coefficient, cm ² /s	Results
Kay and Elrick [1967]	Honeywood silt loam	Organic pesticide (lindane)	3.2 × 10 ⁻⁴ – 6.8 × 10 ⁻⁴	3.6 × 10 ⁻⁵ – 1.1 × 10 ⁻⁴	evidence of nonequilibrium behavior at higher velocity
Lai and Jurinak [1972]	Yolo loam	Na, Ca	1.0 × 10 ⁻³ – 2.0 × 10 ⁻³	7.9 × 10 ⁻⁵ – 2.6 × 10 ⁻⁴	evidence of nonequilibrium behavior
Gupta and Greenkorn [1974]	Otawa sand plus 5% clay	PO ₄	2.5 × 10 ⁻²	3.7 × 10 ⁻²	LEA valid
van Genuchten et al. [1974]	Norge loam	Organic herbicide (picloram)	1.6 × 10 ⁻⁴ – 1.7 × 10 ⁻³	1.7 × 10 ⁻⁵ – 1.3 × 10 ⁻⁴	evidence of nonequilibrium behavior at higher velocity
Hill and Lake [1978]	Berea sandstone	Na, Ca, Mg	3.5 × 10 ⁻⁴ – 7.0 × 10 ⁻⁴	6.4 × 10 ⁻⁵ – 2.0 × 10 ⁻⁴	LEA valid
van Beek and Pal [1978]	Synthetic ion-exchange resin	Na, Ca	2.9 × 10 ⁻⁴	1.0 × 10 ⁻⁵	LEA valid
James and Rubin [1979]	Delhi sand, Oakley sand	Ca	1.7 × 10 ⁻⁵ – 1.7 × 10 ⁻²	3.0 × 10 ⁻⁶ – 3.5 × 10 ⁻²	evidence of nonequilibrium behavior at higher velocity
Persaud and Wierenga [1982]	Synthetic ion-exchange resin	Na, Li, Cs	4.2 × 10 ⁻⁴ – 2.1 × 10 ⁻³	2.2 × 10 ⁻⁵ – 1.6 × 10 ⁻⁴	LEA valid
Reynolds et al. [1982]	Fine sand	Sr, Cs	1.5 × 10 ⁻³ – 1.1 × 10 ⁻²	5.3 × 10 ⁻⁵ – 3.6 × 10 ⁻⁴	evidence of nonequilibrium behavior observed for all conditions
Nkedi-Kizza et al. [1983]	Ione oxisol	³ H ₂ O, ³⁶ Cl	1.4 × 10 ⁻⁴ – 3.0 × 10 ⁻³	5.5 × 10 ⁻⁵ – 2.4 × 10 ⁻³	evidence of nonequilibrium behavior at higher velocity

tween mobile and stagnant fluid zones, while in the third model all of the pore fluid is mobile and the overall sorption rate is governed by the rate of reaction at the soil-solution interfaces. Closed-form analytical solutions to these models are not easily available. Rather than resorting to numerical solutions as did Jennings and Kirkner [1984], we utilize a methodology due to Aris [1958] to derive expressions for the time moments of the solute breakthrough curve. Comparison of the kinetic and equilibrium moment formulas then provides a basis for quantifying the validity of LEA. These results illustrate that the distinction between equilibrium and kinetics depends significantly upon transport system dynamics (e.g., seepage velocity, dispersion coefficients, boundary conditions).

The models to be analyzed in this work are described in the next section; these models are well established in the literature and have been detailed by numerous investigators. This paper does not attempt to assess the relative merits of any particular nonequilibrium model. Our goal is to describe a simple technique for deriving LEA criteria that can be applied to any given kinetic formulation.

TRANSPORT EQUATIONS

A kinetic-based submodel of sorption requires a mathematical description of the microscopic processes that transport the dissolved species to and from the surface where sorption occurs. As was explained by Rubin [1983], such a description is typically based upon a phenomenologically oriented formulation that links macroscopic and microscopic quantities; one popular and successful formulation assumes the reacting interfaces are within a porous "pellet," aggregate, or particle. Weber [1972], Vermeulen et al. [1973], Helfferich [1962], and others have conceptually described the important microscopic rate mechanisms. Based upon this approach, the sorption submodel involves a diffusion equation describing the microscopic concentration profile within the sorbent particle along with an adsorption rate expression and an equation linking the microscopic concentration at the particle boundary to the macroscopic aqueous concentration. The sorbent particle ge-

ometry is most commonly assumed to be spherical. This type of formulation has long been used with great success in the chemical process industry and in the field of wastewater treatment [Vermeulen et al., 1973; Weber, 1972].

As was reviewed by van Genuchten and Cleary [1979] and Rao and Jessup [1983], most models of nonequilibrium adsorption of solutes during flow through soils and aquifers have been based upon assuming that only one of the microscopic mechanisms is rate limiting. These models are usually grouped into two classes: (1) physical nonequilibrium models and (2) chemical nonequilibrium models. In the first group the overall sorption rate is controlled by the rate at which the solute is transported to and from the reacting soil surfaces. In the second group the time dependence of the microscopic transport steps is neglected and the overall sorption rate is equal to the rate of reaction at the soil-solution interfaces.

Physical Nonequilibrium

In this group of models the fluid inside the porous aggregate is assumed stagnant, and thus the total liquid phase is partitioned into mobile (interaggregate) and immobile (intraaggregate) zones. Rao and Jessup [1983], van Genuchten and Cleary [1979], Rao et al. [1980a, b], and others in the soil science field have presented the conceptual foundations of these models. These investigators [see also van Genuchten et al., 1984; van Genuchten, 1985; Nkedi-Kizza et al., 1982] give the following governing transport equation for the case where a certain fraction of the sorption sites can be in contact with the mobile region and where equilibrium sorption in both regions is governed by a linear isotherm:

$$\theta_m R_m \frac{\partial c_m}{\partial t} + \theta_{im} R_{im} \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - \theta_m v \frac{\partial c_m}{\partial x} \quad (1)$$

where the subscripts *m* and *im* refer to parameters for the mobile and immobile regions, respectively, *c* is the aqueous species concentration, θ is porosity, *R* is the retardation factor, *D* is the hydrodynamic dispersion coefficient, *v* is the seepage

velocity, x is distance, and t is time. For spherical aggregate geometry,

$$c_{im} = \frac{3}{a^3} \int_0^a c_a(x, r, t) r^2 dr \quad (2)$$

where c_a is the local aqueous phase concentration inside the aggregate, r is the radial coordinate, and a is the aggregate radius. Continuity of solute concentration at the aggregate boundary is assumed,

$$c_m(x, t) = c_a(x, a, t) \quad (3)$$

Fick's Law along with the assumption of linear equilibrium sorption gives the mass balance equation inside the sphere as

$$R_{im} \frac{\partial c_a}{\partial t} = D_a \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_a}{\partial r} \right) \quad (4)$$

where D_a is an effective molecular diffusion coefficient within the aggregates.

Equations (1) through (4) constitute one of the basic transport models to be analyzed in this paper; henceforth these equations will be referred to as the diffusion physical nonequilibrium model. It will be more convenient to consider the dimensionless form of (1) through (4). The following dimensionless variables are defined [see van Genuchten *et al.*, 1984; van Genuchten, 1985]:

$$T = \frac{vt}{L} \frac{\theta_m}{\theta} \quad (5)$$

$$X = \frac{x}{L} \quad (6)$$

$$P = \frac{vL}{D} \quad (7)$$

$$\xi = \frac{r}{a} \quad (8)$$

$$\gamma = \frac{D_a L \theta_{im}}{a^2 v \theta_m} \quad (9)$$

$$\beta = \frac{\theta_m R_m}{\theta R} \quad (10)$$

where T is a dimensionless time equivalent to the number of pore volumes leached through a soil column of length L , P is the Peclet number, $\theta = \theta_m + \theta_{im}$ is the total porosity, and R is the total retardation factor defined by $\theta R = \theta_m R_m + \theta_{im} R_{im}$. Note that R can also be defined in the standard fashion as $R = 1 + \rho k_d / \theta$, where ρ is the total bulk density of the porous medium, and k_d is the distribution coefficient. Given the above definitions, (1) through (4) becomes

$$\beta R \frac{\partial c_m}{\partial T} + (1 - \beta) R \frac{\partial c_{im}}{\partial T} = \frac{1}{P} \frac{\partial^2 c_m}{\partial X^2} - \frac{\partial c_m}{\partial X} \quad (11)$$

$$c_{im}(X, T) = 3 \int_0^1 c_a(X, \xi, T) \xi^2 d\xi \quad (12)$$

$$c_m(X, T) = c_a(X, 1, T) \quad (13)$$

$$(1 - \beta) R \frac{\partial c_a}{\partial T} = \gamma \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial c_a}{\partial \xi} \right) \quad (14)$$

For simplicity, the subscript m will be dropped from c_m throughout the rest of this paper.

Rao and Jessup [1985] note that γ is a dimensionless rate

parameter and can be considered to be a nonequilibrium index; for "large enough" γ , the diffusion physical nonequilibrium model reduces to

$$R \frac{\partial c}{\partial T} = \frac{1}{P} \frac{\partial^2 c}{\partial X^2} - \frac{\partial c}{\partial X} \quad (15)$$

which is the familiar form of the solute transport equation when LEA is valid. Later in this paper it is shown that the applicability of (15) depends upon other parameters in addition to γ .

In order to avoid geometrical specification of the stagnant region and to simplify the mathematical formulation, several investigators have proposed approximate first-order type rate equations to account for mass exchange between mobile and immobile zones [Coats and Smith, 1964; Baker, 1977; van Genuchten and Wierenga, 1976]. In this approach, (1) is solved along with

$$\theta_{im} R_{im} \frac{\partial c_{im}}{\partial t} = \alpha (c - c_{im}) \quad (16)$$

where α is an empirical mass transfer coefficient that depends in some way upon aggregate geometry and the diffusion coefficient. Rao *et al.* [1980a] and van Genuchten [1985] have derived expressions for α for certain idealized aggregate shapes.

Equations (1) and (16) constitute the second of the basic transport models to be analyzed in this work; these equations will be referred to as the first-order physical nonequilibrium model. The dimensionless form of (16) is

$$(1 - \beta) R \frac{\partial c_{im}}{\partial T} = \omega (c - c_{im}) \quad (17)$$

where $\omega = \alpha L / (v \theta_{im})$ is a dimensionless mass transfer parameter. Hence (11) and (17) constitute the dimensionless form of the first-order physical nonequilibrium model. For large ω , the first-order model approaches the LEA model given by (15).

Chemical Nonequilibrium

In this class of models, no distinction is made between mobile and stagnant liquid regions. Thus the governing solute transport equation is

$$\theta \frac{\partial c}{\partial t} + \rho \frac{\partial s}{\partial t} = D \theta \frac{\partial^2 c}{\partial x^2} - v \theta \frac{\partial c}{\partial x} \quad (18)$$

where s is the sorbed species concentration, ρ is the bulk density of the porous medium, and other parameters are as defined previously. We assume here that the overall sorption rate ($\partial s / \partial t$) can be described as a first-order linear kinetic expression

$$\frac{\partial s}{\partial t} = k_f c - k_r s \quad (19)$$

where k_f and k_r are the forward and reverse rate coefficients for the heterogeneous sorption reaction. Jennings and Kirkner [1984] have recently studied a formulation where (19) is replaced by a nonlinear, Langmuir-type rate expression. The dimensionless form of (18) and (19) is

$$\frac{\partial c}{\partial T} + \frac{\rho}{\theta} \frac{\partial s}{\partial T} = \frac{1}{P} \frac{\partial^2 c}{\partial X^2} - \frac{\partial c}{\partial X} \quad (20)$$

$$\frac{\partial s}{\partial T} = F(k_f c - s) \quad (21)$$

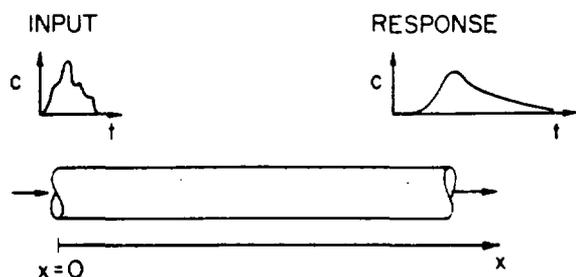


Fig. 1. Schematic representation of solute breakthrough resulting from a pulse input of mass.

where X and P are given by (6) and (7), respectively. T is given by (5) which reduces to $T = vt/L$, since $\theta_m = \theta$, $k_d = k_f$, k_r is the distribution (i.e., equilibrium) coefficient; and F is a dimensionless rate parameter defined by

$$F = k_r L v \quad (22)$$

Equations (20) and (21) constitute the final transport model we will study in this paper; we will refer to these equations as the linear chemical nonequilibrium model.

Nkedi-Kizza *et al.* [1984] describe a two-site chemical nonequilibrium model where sorption on "type 1" sites is governed by linear equilibrium and sorption on "type 2" sites is governed by a first-order rate expression analogous to (19). The two-site model is not explicitly analyzed in this work; however, Nkedi-Kizza *et al.* [1984] have shown that the two-site model is mathematically equivalent to the first-order physical nonequilibrium model given by (11) and (17).

TIME MOMENT ANALYSIS

Although the previously presented models can be solved analytically, the solutions are frequently in the form of integrals that are relatively difficult to evaluate [e.g., Rasmuson and Neretnieks, 1980; Rosen, 1952]. Despite these analytical problems, it is relatively easy to use a method originally described by Aris [1958] to derive expressions for the time moments of the concentration breakthrough curves that would result from any arbitrary pulselike input of mass. Time moments provide useful and physically meaningful descriptors of the concentration breakthrough; for example, the first three time moments would describe the mean breakthrough time, the degree of spreading, and the degree of asymmetry of the concentration response curve, respectively. Time moment analysis is a standard chemical engineering procedure to determine dispersive and rate parameters for packed bed reactors [Turner, 1972; Suzuki and Smith, 1971; Fahim and Wakao, 1982]. Here we use the moment analysis as a tool to characterize the differences between nonequilibrium and equilibrium models of sorbing solute transport.

As is shown schematically in Figure 1, if a soil column is subjected at its influent end to a pulselike input of mass, then the distribution of concentration versus time at any downstream location will also be pulselike. Such a concentration distribution can be described by its absolute moments, defined as

$$m_n = \int_0^t T^n c(X, T) dT \quad (23)$$

where X and T are the dimensionless distance and dimensionless time, respectively. The amount of mass passing any location X is proportional to m_0 ; thus the n th normalized absolute moment can be defined as

$$\mu_n = \frac{m_n}{m_0} = \frac{\int_0^t T^n c(X, T) dT}{\int_0^t c(X, T) dT} \quad (24)$$

The n th central moment is given as

$$\mu_n = \frac{\int_0^t (T - \mu_1)^n c(X, T) dT}{\int_0^t c(X, T) dT} \quad (25)$$

Although the moments can be formally computed if the solution $c(X, T)$ is known, Aris [1958] has shown that under very general conditions

$$m_n = (-1)^n \lim_{p \rightarrow 0} \left[\frac{d^n}{dp^n} \bar{c}(X, p) \right] \quad (26)$$

where $\bar{c}(X, p)$ is the Laplace transform of $c(X, T)$, that is,

$$\bar{c}(X, p) = \int_0^t e^{-pT} c(X, T) dT \quad (27)$$

The power of Aris' method is that it enables computation of the moments from the concentration solution in the Laplace domain, which is often easy to obtain.

Results

The Laplace domain solutions for the previously presented nonequilibrium models are derived in Appendix A. The solutions assume a semi-infinite domain and a Dirac impulse input of mass at the soil column inlet; the initial and boundary conditions are thus

$$c(X, T = 0) = s(X, T = 0) = c_{im}(X, T = 0) = 0 \quad (28)$$

$$c(X \rightarrow \infty, T) = s(X \rightarrow \infty, T) = c_{im}(X \rightarrow \infty, T) = 0 \quad (29)$$

$$\left(c - \frac{1}{P} \frac{\partial c}{\partial X} \right) \Big|_{x=0} = A \delta(T) \quad (30)$$

In (30), $\delta(T)$ is the Dirac Delta function and $A = M(\theta L)$, where M is the mass input per unit column cross-sectional area, since, by definition,

$$M = \int_0^t \left(v \theta_m c - D \theta_m \frac{\partial c}{\partial X} \right) \Big|_{x=0} dt \quad (31)$$

For the linear chemical nonequilibrium model, θ_m in (31) is equivalent to θ .

Several investigators have demonstrated that the solutions derived in Appendix A do not directly apply to solute concentrations measured in the effluent of a column leaching experiment [Brigham, 1974; Kreft and Zuber, 1978; van Genuchten *et al.*, 1984; Parker and van Genuchten, 1984]. These studies have shown that a proper description is obtained by applying a mass balance condition at the end of the soil column ($X = 1$)

$$c_d(T) = \left(c - \frac{1}{P} \frac{\partial c}{\partial X} \right) \Big|_{x=1} \quad (32)$$

The variable c_e is usually denoted the flowing or flux concentration, whereas c is termed the in situ or resident concentration. The flux concentration can be defined at any location in the soil column and can be interpreted as the ratio of the solute mass flux to the fluid volume flux (specific dis-

TABLE 2 Time Moment Formulas for Equilibrium and Nonequilibrium Models, Dirac Input

Moment	Local Equilibrium	Physical Nonequilibrium		Chemical Nonequilibrium, Linear
		Diffusion	First Order	
μ_1	$\frac{XR}{P}$	$\frac{XR}{P}$	$\frac{XR}{P}$	$\frac{XR}{P}$
μ_2	$\frac{2XR^2}{P}$	$\frac{2XR^2}{P} - \frac{2}{15} \frac{X(1-\beta)^2 R^2}{P}$	$\frac{2XR^2}{P} + \frac{2X(1-\beta)^2 R^2}{\omega}$	$\frac{2XR^2}{P} - \frac{2X(R-1)}{F}$
μ_3	$\frac{12XR^3}{P^2}$	$\frac{12XR^3}{P^2} - \frac{4}{5} \frac{X(1-\beta)^2 R^3}{P}$ $+ \frac{4}{105} \frac{X(1-\beta)^3 R^3}{P}$	$\frac{12XR^3}{P^2} + \frac{12X(1-\beta)^2 R^3}{P\omega}$ $+ \frac{6X(1-\beta)^3 R^3}{\omega^2}$	$\frac{12XR^3}{P^2} - \frac{12XR(R-1)}{PF}$ $+ \frac{6X(R-1)}{F^2}$

charge). Applying (32) to the diffusion physical nonequilibrium solution (A13) gives

$$\bar{c}_d(X, p) = A \exp \left[\frac{XP}{2} \left(1 - \left(1 - \frac{4}{P} (\beta R p + G(p)) \right)^{1/2} \right) \right] \quad (33)$$

where $G(p)$ is defined by (A12). Likewise, the Laplace transform of the flux concentration for the first-order physical nonequilibrium model (A18) is

$$\bar{c}_d(X, p) = A \exp \left[\frac{XP}{2} \left(1 - \left(1 - \frac{4}{P} (\beta R p + H(p)) \right)^{1/2} \right) \right] \quad (34)$$

where $H(p)$ is defined by (A17), and for the linear chemical nonequilibrium model (A19) is

$$\bar{c}_d(X, p) = A \exp \left[\frac{XP}{2} \left(1 - \left(1 - \frac{4P}{P} \left(1 - \frac{F(R-1)}{p+F} \right) \right)^{1/2} \right) \right] \quad (35)$$

The subscript e will be dropped, since only flux concentrations are considered in the remainder of this paper. In the limit, as the appropriate rate parameters (ω , F) get large, the nonequilibrium solutions approach

$$c_d(X, p) = A \exp \left[\frac{XP}{2} \left(1 - \left(1 + \frac{4R}{P} p \right)^{1/2} \right) \right] \quad (36)$$

which is the Laplace domain solution of the LEA model (15).

The Laplace domain solutions, (33) through (36), can be differentiated according to (26) in order to compute the time moments of the concentration breakthrough curve at any arbitrary location X . The details of this differentiation and limiting procedure are straightforward but become tedious for the higher order moments; these details are not reported here. The final expressions for the first three central moments are given in Table 2. These results tend to corroborate the findings of previous theoretical studies and laboratory column experiments: namely, that sorption rate limitations are generally manifested by an enhanced spreading and tailing (i.e., increased second and third central moment) of solute breakthrough curves. The expressions in Table 2 demonstrate that at least for the models postulated in this study, nonequilibrium does not influence the mean breakthrough time of the solute pulse. Table 2 also shows a striking similarity among the time moment expressions for the various nonequilibrium models; this suggests that the general shape of solute break-

through curves is not very sensitive to the form of the kinetic submodel.

The expressions in Table 2 provide a basis for quantifying the effects of rate limitations and evaluating the validity of LEA, since nonequilibrium and equilibrium breakthrough curves will be essentially indistinguishable from one another when their respective moments are approximately equal. As is expected from Table 2 and the mathematical formulation of the kinetic submodels, the nonequilibrium breakthrough curves approach the equilibrium breakthrough curves when the dimensionless rate parameter increases. This is demonstrated for the linear chemical nonequilibrium model in Figure 2 which compares the equilibrium and nonequilibrium breakthrough curves at $X = 1$ for the case with $P = 10$ and $R = 4$. The equilibrium breakthrough curve is given by the inverse of (36) which is reported by *DeSmedt and Wierenga* [1979] and *Kreft and Zuber* [1978] as

$$C(X, T) = \left(\frac{PR}{4\pi T^3} \right)^{1/2} X \exp \left\{ -\frac{PR}{4T} \left(X - \frac{T}{R} \right)^2 \right\} \quad (37)$$

where $C(X, T)$ is a relative concentration defined as

$$C = \frac{c}{A} = \frac{c}{M(\theta L)} \quad (38)$$

The quantity $M(\theta L)$ is the dissolved solute concentration that would be attained if the total mass input were uniformly distributed throughout the soil column pore volume; the definition (38) is commonly utilized in chemical engineering studies (see, for example, *Levenspiel and Bischoff* [1963]). In the studies of *DeSmedt and Wierenga* [1979] and *van Genuchten* [1981], (35) is inverted analytically, and the result is presented as an integral involving modified Bessel functions. However, the analytical inverse was found to yield anomalous results for large values of F ; consequently, the nonequilibrium results in Figure 2 were calculated by numerically inverting the Laplace transform (35). To enhance the reliability of the calculated results, two different inversion algorithms were utilized, one due to *Durbin* [1974], the other due to *Stehfest* [1970]. The latter algorithm has been recently applied to solute transport problems by *Moench and Ogata* [1981]. For the curves presented in this paper the two methods gave results that generally agreed to within a few percent. The curves displayed in Figure 2 clearly illustrate that LEA becomes more applicable as F increases for fixed values of P and R . For most practical purposes we could say that LEA is certainly valid when $F \geq 100$ for the conditions of Figure 2.

The differences among the curves in Figure 2 are logically reflected in the computed values for the moments; the values for μ_2 and μ_3 as computed from the appropriate formulas of

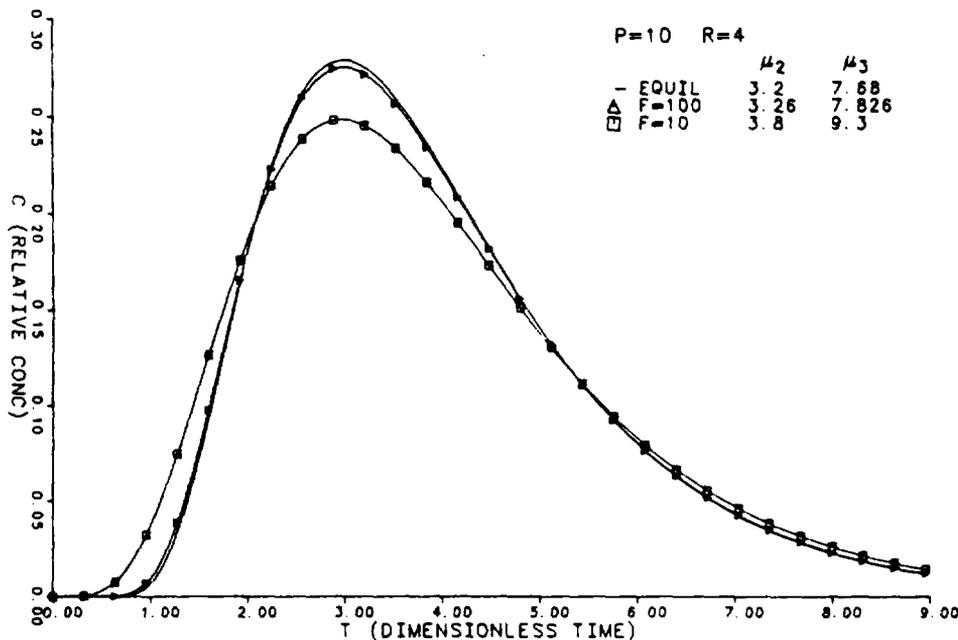


Fig. 2. Comparison of equilibrium and linear chemical nonequilibrium breakthrough curves at $X = 1$ for $P = 10$ and $R = 4$. Mass input at $X = 0$ is a Dirac impulse.

Table 2 are also given in Figure 2. Defining ϵ_n , the fractional change in the n th central moment, as

$$\epsilon_n = \frac{\mu_n^K - \mu_n^E}{\mu_n^E} \quad (39)$$

where the superscripts K and E refer to the kinetic (i.e., nonequilibrium) and equilibrium models, respectively, we can compute $\epsilon_2 = 0.02$ and $\epsilon_3 = 0.02$ for the $F = 100$ breakthrough and $\epsilon_2 = 0.19$ and $\epsilon_3 = 0.21$ for the $F = 10$ breakthrough. In the context of the time moment analysis, the question of LEA validity gives rise to two fundamental issues: first, how does ϵ_n depend upon system parameters, and second, how large can ϵ_n be before the solute breakthrough exhibits severe deviations from local equilibrium. The latter issue is beyond the scope of this paper; however, it could possibly be addressed by interpreting the solute breakthrough curve as a probability density function and subsequently applying one of the well-known series expansions of an arbitrary density function in terms of its moments [see Kendall and Stuart, 1977, chapter 6]. These series expansions have been applied to solute transport problems by numerous investigators, including Gelhar et al. [1979], Kucera [1965], Wiedemann et al. [1978], and Razavi et al. [1978].

The former issue, the effect of system parameters upon ϵ_n , can be easily addressed with the time moment formulas of Table 2. Substituting the appropriate expression from Table 2 into (39) yields for the linear chemical nonequilibrium model

$$\epsilon_2 = \frac{P(R-1)}{F R^2} \quad (40)$$

$$\epsilon_3 = \frac{P(R-1)}{F R^2} \left(1 + \frac{P}{F 2R} \right) \quad (41)$$

The corresponding results for the diffusion physical nonequilibrium model are

$$\epsilon_2 = \frac{P}{\gamma} \frac{1}{15} (1 - \beta)^2 \quad (42)$$

$$\epsilon_3 = \frac{P}{\gamma} \frac{1}{15} (1 - \beta)^2 \left(1 + \frac{P(1 - \beta)}{\gamma 21} \right) \quad (43)$$

and for the first-order physical nonequilibrium model are

$$\epsilon_2 = \frac{P}{\omega} (1 - \beta)^2 \quad (44)$$

$$\epsilon_3 = \frac{P}{\omega} (1 - \beta)^2 \left(1 + \frac{P(1 - \beta)}{\omega 2} \right) \quad (45)$$

Since solute breakthrough will exhibit greater deviations from equilibrium conditions as ϵ_n increases, the preceding equations describe the influence of system parameters upon LEA validity. The results (40)–(45) are consistent with the previously noted fact that equilibrium is approached as the dimensionless rate (F , γ , ω) increases for fixed values of P , R and β ; however, these equations indicate that the approach to equilibrium also depends upon the porous medium's dispersive (P) and equilibrium sorptive (R , β) properties. As an example, the results specify the crucial role played by the ratio P/F for the linear

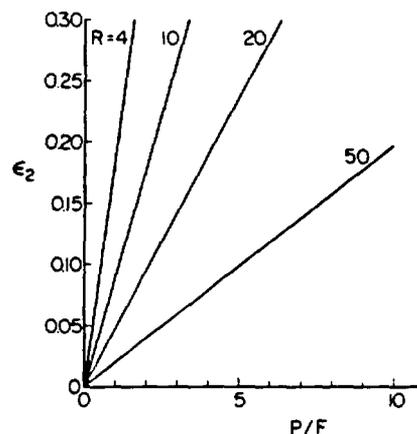


Fig. 3. Dependence of ϵ_2 upon P , F , and R for the linear chemical nonequilibrium model and a Dirac input.

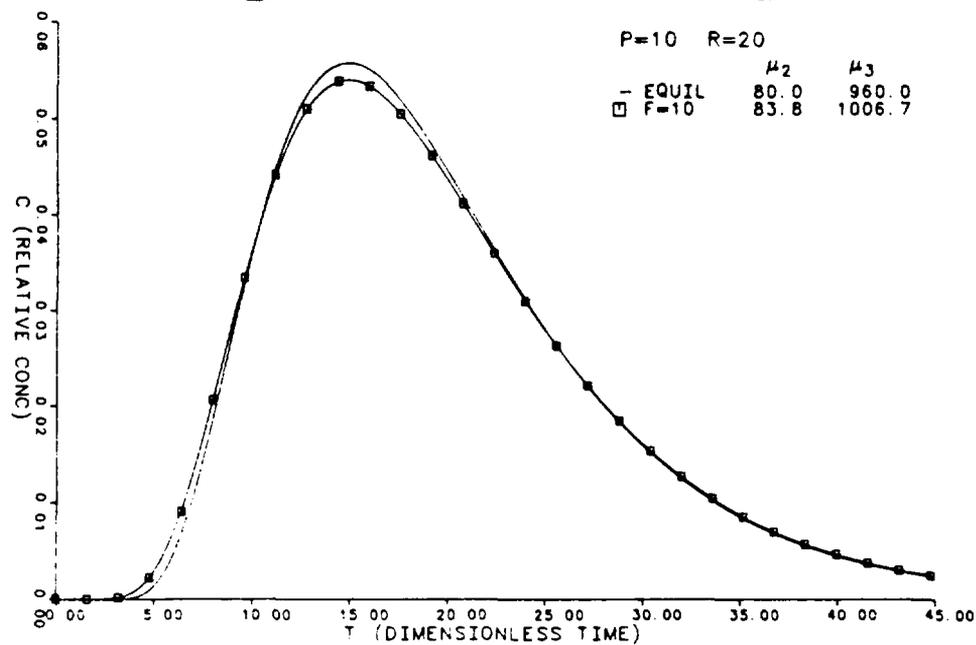


Fig. 4. Comparison of equilibrium and linear chemical nonequilibrium breakthrough curves at $X = 1$ for $P = 10$ and $R = 20$. Mass input at $X = 0$ is a Dirac impulse.

chemical nonequilibrium model; for fixed R values P/F is an index of nonequilibrium behavior. This is demonstrated in Figure 3, which is a plot of (40). The key point is that the question of whether or not LEA is valid does not have a simple answer: the answer depends upon all system parameters as well as upon the assumed form of the nonequilibrium submodel.

The linear chemical nonequilibrium model can be used to illustrate some of the above-mentioned parameter influences. Figure 4 shows the equilibrium and nonequilibrium breakthrough at $X = 1$ for $P = 10$, $F = 10$, and $R = 20$; these results were obtained with the previously discussed numerical Laplace transform inverters. Comparison with the $F = 10$ curve in Figure 2 dramatically shows the influence of increas-

ing the retardation factor: increasing R from 4 to 20 decreases ϵ_2 from 0.19 to approximately 0.05 (see also Figure 3). The deviation between the equilibrium and $F = 10$ curves in Figure 4 is thus significantly smaller than in Figure 2.

Figure 5 shows the breakthrough results for $P = 100$ and $R = 4$; the nonequilibrium curves for $F = 1000$ and $F = 100$ have the same P/F ratios as the $F = 100$ and $F = 10$ curves in Figure 2 where $P = 10$. Hence the ϵ_2 and ϵ_3 values for $F = 1000$ in Figure 5 are identical to those for $F = 100$ in Figure 2. A similar equality applies between $F = 100$ in Figure 5 and $F = 10$ in Figure 2. Comparing the $F = 100$ curves in Figures 2 and 5 demonstrates that the linear chemical nonequilibrium model approaches local equilibrium as P decreases, for fixed F and R .

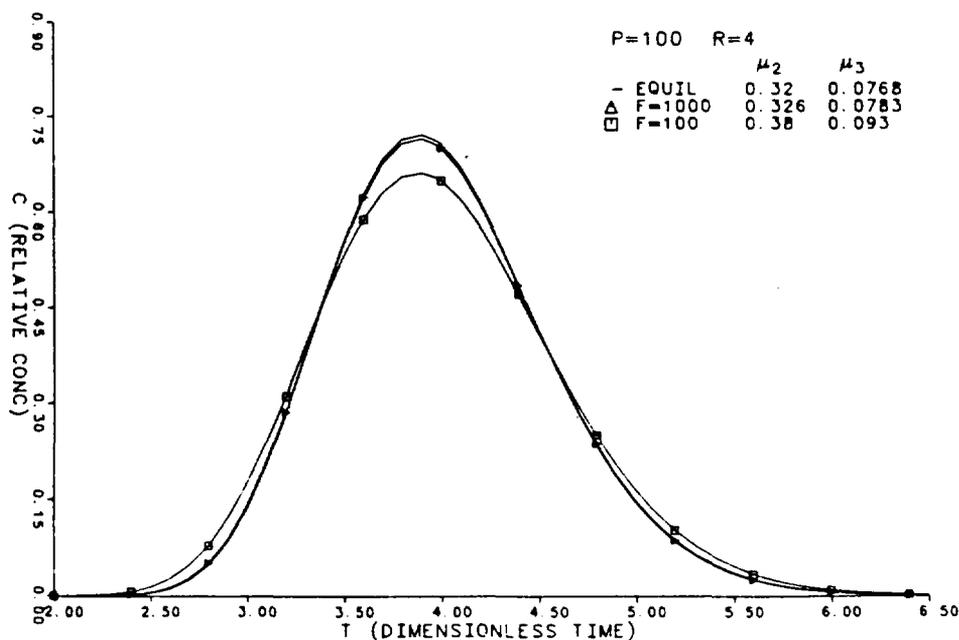


Fig. 5. Comparison of equilibrium and linear chemical nonequilibrium breakthrough curves at $X = 1$ for $P = 100$ and $R = 4$. Mass input at $X = 0$ is a Dirac Impulse.

Figure 5 also illustrates that the solute breakthrough curves become more symmetrical as P increases. This feature is consistent with the moment formulas in Table 2 which show that an increase in P will generally cause μ_3 (skewness) to diminish with respect to μ_2 (variance). It is possible to demonstrate theoretically that the LEA breakthrough curve described by (37) approaches a Gaussian distribution with mean XR and variance $2XR^2/P$ as P increases (see, for example, Turner [1972] and Suity [1980]). For dimensionless rate values that are not "too small" the nonequilibrium breakthrough will also be approximately Gaussian. This suggests the possibility of using analytical properties of the normal probability function to develop quantitative criteria for LEA validity. As is stated above, the solute breakthrough curves for large P values can be approximated as

$$C(X, T) \approx \frac{1}{(\sqrt{2\pi}\mu_2)^{1/2}} \exp\left[-\frac{(T - XR)^2}{2\mu_2}\right] \quad (46)$$

where μ_2 is given in Table 2. The maximum solute concentration will thus occur at a time $T = XR$ and be equal to $(2\pi\mu_2)^{-1/2}$. In analogy to (39), the fractional change in the maximum solute concentration can be defined as

$$\epsilon_{\max} = \frac{C_{\max}^E - C_{\max}^K}{C_{\max}^E} = 1 - \left(\frac{\mu_2^K}{\mu_2^E}\right)^{1/2} \quad (47)$$

where the superscripts E and K refer to the equilibrium and kinetic models, respectively. Equation (47) can be combined with (39) to yield

$$\epsilon_{\max} = 1 - \left(\frac{1}{1 + \epsilon_2}\right)^{1/2} \quad (48)$$

where ϵ_2 is given by (40), (42), or (44). The result (48) represents one way to quantitatively describe the influence of parameter values upon deviations from local equilibrium. As an example, for the linear chemical nonequilibrium model (48) can be used to answer the question, How small can F be before ϵ_{\max} becomes greater than some specified tolerance? The validity of (48) can be tested with the results in Figure 5 despite the fact that the curves displayed there are not precisely Gaussian. For $F = 100$, $P = 100$, and $R = 4$, $\epsilon_2 = 0.19$ (see Figure 3); hence (48) predicts $\epsilon_{\max} = 0.083$. The numerical data used to plot Figure 5 reveals $C_{\max}^E \approx 0.72$ and $C_{\max}^K \approx 0.66$ yielding a computed $\epsilon_{\max} = 0.083$, which is identical to the value predicted by (48).

The normal probability distribution is completely specified by two parameters, the mean and the variance. Therefore if the nonequilibrium breakthrough curves shown in Figure 5 are approximately Gaussian, then they can be described by an advection-dispersion type of equation. That is, an additional set of kinetic submodel equations is not required. This point is discussed further in the following section.

An Effective Dispersion Approach

The models described in this paper consist of an advection-dispersion equation for transport along the soil column plus an additional equation explicitly accounting for solute transfer between the aqueous and sorbed states. However, Passioura [1971], Baker [1977], and others studying the problem of nonreactive solute movement through media containing dead-end pores have shown theoretically that the additional kinetic equation is not required to describe breakthrough from long soil columns, provided that the dispersion coefficient is modified to reflect the source-sink effects of mass transfer into and

out of the stagnant pores. Rao *et al.* [1980b] and DeSmedt and Wierenga [1984] have recently applied this effective dispersion coefficient approach to tracer movement in saturated and unsaturated laboratory columns. Pickens *et al.* [1981] compared field breakthrough curves for nonreactive and reactive solutes and observed that nonequilibrium effects could be modeled with a modified dispersion coefficient. These observations are consistent with Figure 5 which demonstrates that the solute breakthrough curves become Gaussian as P increases.

The time moment analysis explicitly shows the effect of parameters upon the variance of the solute breakthrough curve. Therefore it is a simple task to utilize the expressions in Table 2 to derive effective dispersion coefficients. Modifying the results of Aris [1958] and Turner [1972] for the dimensionless variable definitions used in this paper, we can show that

$$\frac{v_{eff}}{v} = X \frac{\theta_m}{\theta} (\mu_1)^{-1} \quad (49)$$

$$\frac{1}{P_{eff}} = \frac{D_{eff}}{vL} = \frac{1}{2} \left(\frac{\theta}{\theta_m}\right) \left(\frac{\mu_2}{\mu_1}\right) \left(\frac{v_{eff}}{v}\right)^2 \quad (50)$$

where the moments are those listed in Table 2. (Note that $\theta = \theta_m$ for the linear chemical nonequilibrium model). Thus solute transport through long soil columns (large P) is governed by an advection-dispersion equation with an effective velocity given by (49) and an effective dispersion coefficient given by (50). Table 2 indicates that the equilibrium and nonequilibrium models have the same v_{eff} .

$$v_{eff} = \frac{v}{R} \frac{\theta_m}{\theta} \quad (51)$$

whereas the equilibrium model has

$$D_{eff} = \frac{D}{R} \frac{\theta_m}{\theta} \quad (52)$$

the diffusion physical nonequilibrium model has

$$D_{eff} = \frac{D}{R} \frac{\theta_m}{\theta} + \frac{(1 - \beta)^2 (\alpha v \theta_m)^2}{15 D_s R \theta \theta_{im}} \quad (53)$$

the first-order physical nonequilibrium model has

$$D_{eff} = \frac{D}{R} \frac{\theta_m}{\theta} + \frac{(1 - \beta)^2 (\theta_m v)^2}{R \alpha \theta} \quad (54)$$

and the linear chemical nonequilibrium model has

$$D_{eff} = \frac{D}{R} + \left(\frac{v}{R}\right)^2 \frac{(R - 1)}{R} \frac{1}{f} \quad (55)$$

Analytical solutions to the advection-dispersion equation with the above noted effective velocity and dispersion coefficients have been compared to linear chemical nonequilibrium breakthrough curves computed by numerical inversion of (35). The two solutions agree very closely over a wide range of F values, provided P is large enough; in this work, $P > 1000$ proved sufficient. This P value is in the same range as that reported by Baker [1977] and DeSmedt and Wierenga [1984].

Non-Dirac Inputs

As previously noted, LEA is generally valid when the rate of change of solute mass due to the microscopic sorption processes is much faster than that due to the bulk flow process. Therefore LEA validity should depend upon the time vari-

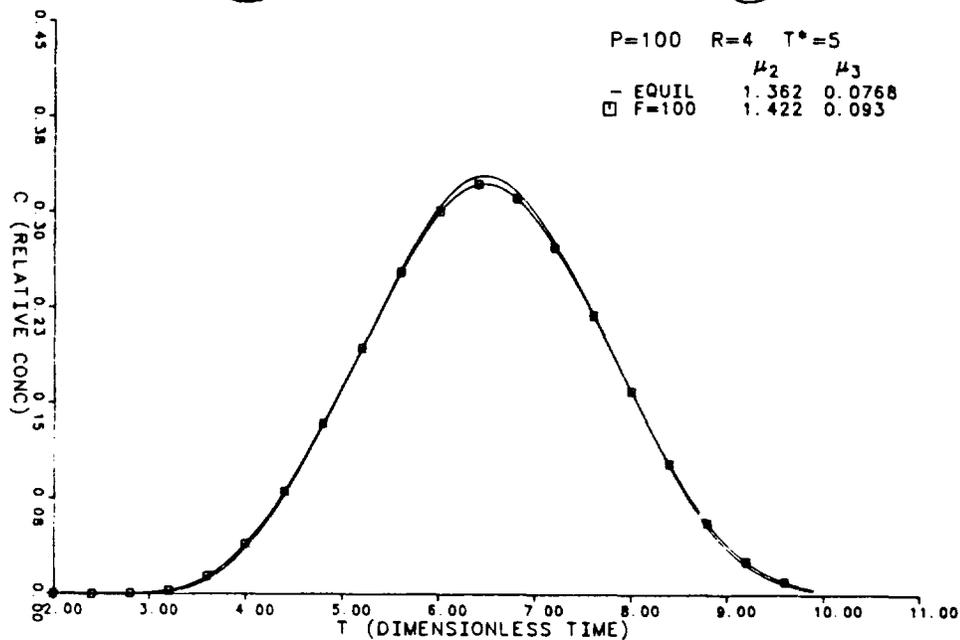


Fig. 6. Comparison of equilibrium and linear chemical nonequilibrium breakthrough curves at $X = 1$ for $P = 100$ and $R = 4$. Mass input at $X = 0$ is a symmetrical triangular function with base, T^* , equal to 5 and height equal to $2T^*$.

ation of the mass input function as well as the relative magnitude of the seepage velocity, dispersion coefficient, and sorption rate parameters. The time moment analysis can be easily extended to cases of non-Dirac pulse inputs of mass. For this case, the boundary condition (30) becomes

$$\left(c - \frac{1}{P} \frac{\partial c}{\partial X} \right) \Big|_{X=0} = Af(T) \quad (56)$$

As in the Dirac input situation, $A = M(\theta L)$, where M is the total mass input per unit column cross-sectional area. According to (56), the total mass is input over time according to the function $f(T)$. In order for the solute breakthrough curve to be pulslike, $f(T)$ must also have the general form of a pulse; that is, $f(T)$ must rise from zero and return to zero after some finite time (see Figure 1). Mass balance arguments also show that $f(T)$ must satisfy

$$\int_0^{\infty} f(T) dT = 1 \quad (57)$$

The Dirac input condition (30) can thus be viewed as a special case of the general pulse input condition (56).

Expressions for the time moments of the solute breakthrough curves resulting from a mass input described by (56) can easily be derived from the expressions previously defined in Table 2 for a Dirac input. It is shown in Appendix B that the time moments of solute breakthrough for the two different inputs are related by

$$\mu_1^f = \mu_1^\delta + v_1 \quad (58)$$

$$\mu_n^f = \mu_n^\delta + v_n \quad n = 2, 3 \quad (59)$$

where the f and δ superscripts refer to the general pulse input and the Dirac input, respectively; v_1 is the first absolute moment (mean) of the input function $f(T)$; and v_n is the n th central moment of $f(T)$ (see equations (23)–(25)). Therefore the general pulse moments are given by the expressions in Table 2 plus the appropriate moment of the input function.

In order to examine the implications of non-Dirac inputs,

we will take $f(T)$ to be a symmetrical triangular function with base width equal to T^* . This simple functional form has mean (v_1) equal to $T^*/2$, variance (v_2) equal to $T^{*2}/24$, and skewness (v_3) equal to zero. Hence the values of μ_1 and μ_2 for both the equilibrium and nonequilibrium models are increased by these amounts; that is, the equilibrium breakthrough curve has

$$\mu_2 = \frac{2XR^2}{P} + \frac{T^{*2}}{24} \quad (60)$$

and the linear chemical nonequilibrium breakthrough curve has

$$\mu_2 = \frac{2XR^2}{P} + \frac{2X(R-1)}{F} + \frac{T^{*2}}{24} \quad (61)$$

Thus spreading of the breakthrough curve will reflect the effects of the non-Dirac input function as well as the parameters P , R , and F . As before, we can use differences between the equilibrium and nonequilibrium moments as an index of LEA validity. By using definition (39), we find the linear chemical nonequilibrium model has

$$\varepsilon_2 = \frac{P}{F} \left(\frac{R-1}{R^2} \right) \left(1 + \frac{PT^{*2}}{48XR^2} \right)^{-1} \quad (62)$$

Comparing (62) with the result (40) for the Dirac input, we conclude that deviations from local equilibrium behavior should become less significant as the solute mass is input gradually over longer and longer time intervals. As is demonstrated in (62), the importance of a nonzero T^* depends upon the magnitude of P , X , and R .

The effects of non-Dirac mass inputs can also be visualized by examining solute breakthrough curves resulting from the symmetrical triangular input. These breakthrough curves can be computed with the previously mentioned numerical Laplace transform inversion algorithms. The Laplace domain

solution for the linear chemical nonequilibrium model is (see Appendix B)

$$\bar{c}(X, p) = A \bar{f}(p) \exp \left[\frac{XP}{2} \left(1 - \left(1 + \frac{4p}{P} \left(1 + \frac{F(R-1)}{p+F} \right) \right)^{1/2} \right) \right] \quad (63)$$

where $\bar{f}(p)$ is the Laplace transform of the triangular input function. With the aid of Abramowitz and Stegun [1972, p. 1025], we can calculate $\bar{f}(p)$ as

$$\bar{f}(p) = \frac{4}{T^*} \frac{1}{p^2} \tanh \left(\frac{T^* p}{4} \right) (1 - e^{-T^* p}) \quad (64)$$

The inverse of (63) is plotted in Figure 6 as relative concentration versus T at $X = 1$ for $T^* = 5$, $P = 100$, and $R = 4$. The equilibrium breakthrough curve was computed by using very large F values in (63). Comparison of Figures 6 and 5 show that deviations from local equilibrium for the Dirac input are much more pronounced than those for the triangular input. This agrees with (62) which shows that ϵ_2 for the $F = 100$ curve decreases from 0.19 for the Dirac input (Figure 5) to 0.045 for the triangular input (Figure 6).

DISCUSSION AND CONCLUSIONS

It is generally recognized that LEA is valid when the rate of change of solute mass due to the microscopic sorption processes is "much faster" than that due to the bulk flow processes. This study shows that this qualitative statement can be quantified for any given kinetic formulation. By analyzing expressions for the time moments of sorbing solute breakthrough curves, we derived criteria for LEA validity in one-dimensional, steady flow through homogeneous soils. These criteria are given by (40) through (45). Even for the simple models postulated here, the issue of LEA validity depends upon a complex interplay between macroscopic transport properties (seepage velocity, hydrodynamic dispersion, time variation of mass input) and microscopic sorption properties (e.g., mass transfer coefficient, aggregate size, distribution coefficient). The results derived in this paper depend additionally upon the assumed nonequilibrium submodel. Also, as was noted by Rubin [1983], the distinction between equilibrium and kinetics is pragmatic rather than fundamental. Figures 2 through 5 demonstrate that kinetic breakthrough curves smoothly approach the LEA curve as appropriate parameters change in the proper fashion: the point at which LEA is deemed "valid" depends upon some subjective assessment of permissible error. This allowable level of error is likely to be larger in a practical field problem than in a theoretical laboratory experiment.

The time moment methodology utilized in this study is a powerful tool for characterizing the behavior of mathematical models of sorbing solute transport. Because analytical solution of the coupled differential equations that typically comprise such models is not necessary, the method can be readily applied to a wide variety of nonequilibrium formulations. For example, Kucera [1965] has used the time moment method to analyze a very general model accounting for film diffusion, internal diffusion within a porous spherical aggregate, and kinetically controlled adsorption onto the internal aggregate surfaces. However, the time moment analysis is restricted to linear problems, since it relies upon the Laplace transform of the model solution.

Although we have only analyzed one-dimensional, steady

flow through homogeneous soil columns, our results have some interesting implications for practical field problems. For example, while a kinetic sorption model may be necessary for nearly instantaneous contaminant inputs (e.g., a spill), LEA may be valid for describing transport from a hazardous waste landfill where the pollutants may be input more gradually over time.

In conclusion, it should be noted that the LEA criteria developed in this study are strongly dependent upon the form of the hypothesized kinetic model. In order for the derived criteria to be practically useful, the conceptual model of the nonequilibrium processes must have a sound scientific basis so that the sorption parameters are physically meaningful and measurable.

APPENDIX A: TRANSPORT MODEL SOLUTIONS IN THE LAPLACE DOMAIN

Diffusion Physical Nonequilibrium

The basic diffusion physical nonequilibrium model is given by (11) through (14), which are subject to the initial and boundary conditions (28) through (30). The definition of the Laplace transform given by (27) can be used in (11), (12), and (14) to give

$$\frac{1}{P} \frac{d^2 \bar{c}}{dX^2} - \frac{d\bar{c}}{dX} - \beta R p \bar{c} - (1 - \beta) R p \bar{c}_{im} = 0 \quad (A1)$$

$$\bar{c}_{im} = 3 \int_0^1 \bar{c}_a \xi^2 d\xi \quad (A2)$$

$$(1 - \beta) R p \bar{c}_a = \gamma \frac{1}{\xi^2} \frac{d}{d\xi} \left(\xi^2 \frac{d\bar{c}_a}{d\xi} \right) \quad (A3)$$

respectively. The boundary conditions (29) and (30) will transform to

$$\bar{c}(X \rightarrow \infty, p) = 0 \quad (A4)$$

$$\left(\bar{c} - \frac{1}{P} \frac{d\bar{c}}{dX} \right) \Big|_{X=0} = A \quad (A5)$$

and condition (13) will transform to

$$\bar{c}(X, p) = \bar{c}_a(X, \xi = 1, p) \quad (A6)$$

Equation (A3) can be combined with (A2) to yield an expression for \bar{c}_{im} , which when substituted into (A1) gives

$$\frac{1}{P} \frac{d^2 \bar{c}}{dX^2} - \frac{d\bar{c}}{dX} - \beta R p \bar{c} - 3\gamma \left(\frac{d\bar{c}_a}{d\xi} \right) \Big|_{\xi=1} = 0 \quad (A7)$$

Next, the aggregate mass balance equation (A3) can be written as

$$z^2 \frac{d^2 \bar{c}_a}{dz^2} + 2z \frac{d\bar{c}_a}{dz} - z^2 \bar{c}_a = 0 \quad (A8)$$

where $z = \xi(p/\gamma)^{1/2}$ and $\gamma = \gamma_0 [R(1 - \beta)]$. Equation (A8) possesses solutions in the form of modified spherical Bessel functions [Abramowitz and Stegun, 1972]. The solution that is finite at $\xi = 0$, when combined with the condition (A6) will yield

$$\bar{c}_a(X, \xi, p) = \frac{\bar{c}(X, p)}{\left(\frac{\pi}{2} \right)^{1/2} \left(\frac{z}{p} \right)^{1/4} I_{1/2} \left(\left(\frac{p}{\gamma} \right)^{1/2} z \right)}$$

$$\left(\frac{\pi}{2z}\right)^{1/2} \left(\frac{z}{p}\right)^{1/4} I_{1/2}\left(\frac{p}{z}\right)^{1/2} \quad (\text{A9})$$

where $I_{1/2}$ is the modified spherical Bessel function of the first kind. From the solution (A9) we can calculate

$$\frac{d\bar{c}_a}{d\bar{z}} = \frac{\bar{c}(X, p)}{\sinh\left(\left(\frac{p}{z}\right)^{1/2}\right)} \frac{p}{z} \left(\frac{\cosh\left(\zeta\left(\frac{p}{z}\right)^{1/2}\right)}{\zeta\left(\frac{p}{z}\right)^{1/2}} - \frac{\sinh\left(\zeta\left(\frac{p}{z}\right)^{1/2}\right)}{\zeta^2\frac{p}{z}} \right) \quad (\text{A10})$$

where we have used the identity

$$\left(\frac{\pi}{2z}\right)^{1/2} I_{1/2}(z) = \frac{\sinh z}{z}$$

When (A10) is evaluated at $\bar{z} = 1$ and substituted into (A7) the result is

$$\frac{1}{P} \frac{d^2\bar{c}}{dX^2} - \frac{d\bar{c}}{dX} - [\beta R p + G(p)]\bar{c} = 0 \quad (\text{A11})$$

where

$$G(p) = 3\gamma\left(\frac{p}{z}\right)^{1/2} \coth\left(\frac{p}{z}\right)^{1/2} - 1 \quad (\text{A12})$$

The solution of (A11) satisfying the boundary conditions (A4) and (A5) is

$$\bar{c}(X, p) = \frac{2A}{1 + \left\{1 + \frac{4}{P} [\beta R p + G(p)]\right\}^{1/2}} \cdot \exp\left[\frac{XP}{2} \left(1 - \left(1 + \frac{4}{P} [\beta R p + G(p)]\right)^{1/2}\right)\right] \quad (\text{A13})$$

First-Order Physical Nonequilibrium

This model consists of (11) and (17) subject to the conditions (28) through (30). Taking the Laplace transform of (11) and (17) yields

$$\frac{1}{P} \frac{d^2\bar{c}}{dX^2} - \frac{d\bar{c}}{dX} - \beta R p \bar{c} - (1 - \beta) R p \bar{c}_{im} = 0 \quad (\text{A14})$$

$$(1 - \beta) R p \bar{c}_{im} = \omega(\bar{c} - \bar{c}_{im}) \quad (\text{A15})$$

respectively. When (A15) is substituted into (A14), the result is

$$\frac{1}{P} \frac{d^2\bar{c}}{dX^2} - \frac{d\bar{c}}{dX} - (\beta R p + H(p))\bar{c} = 0 \quad (\text{A16})$$

where

$$H(p) = \frac{(1 - \beta) R \omega p}{(1 - \beta) R p + \omega} \quad (\text{A17})$$

The solution of (A16) subject to boundary conditions (A4) and (A5) is

$$\bar{c}(X, p) = \frac{2A}{1 + \left[1 + \frac{4}{P} (\beta R p + H(p))\right]^{1/2}}$$

$$\cdot \exp\left[\frac{XP}{2} \left(1 - \left(1 + \frac{4}{P} (\beta R p + H(p))\right)^{1/2}\right)\right] \quad (\text{A18})$$

Linear Chemical Nonequilibrium

This model is given by (20) and (21). Proceeding as in the previous analyses, the appropriate Laplace domain solution is found to be

$$\bar{c}(X, p) = \frac{2A}{1 + \left[1 + \frac{4p}{P} \left(1 + \frac{F(R-1)}{p+F}\right)\right]^{1/2}} \cdot \exp\left[\frac{XP}{2} \left(1 - \left(1 + \frac{4p}{P} \left(1 + \frac{F(R-1)}{p+F}\right)\right)^{1/2}\right)\right] \quad (\text{A19})$$

APPENDIX B: RELATION BETWEEN TIME MOMENTS FOR DIRAC INPUT AND GENERAL PULSE INPUT

From Appendix A, the general Laplace-domain solution to the nonequilibrium models can be expressed in the form

$$\bar{c}(X, p) = B e^{\lambda(p)X} \quad (\text{B1})$$

where B is an arbitrary constant fixed by the boundary condition at $X = 0$. For a Dirac input, boundary condition (30) for c transforms to (A5) for \bar{c} , thus giving $B = A/[1 - \lambda(p)/P]$. Equation (B1) can thus be written

$$\bar{c}^\delta = \frac{A}{1 - \frac{\lambda(p)}{P}} e^{\lambda(p)X} \quad (\text{B2})$$

where the superscript δ denotes the Dirac input solution.

For a general pulse input, the Laplace transform of boundary condition (56) is

$$\left(\bar{c} - \frac{1}{P} \frac{d\bar{c}}{dX}\right)\Big|_{X=0} = A \bar{f}(p) \quad (\text{B3})$$

where $\bar{f}(p)$ is the Laplace transform of the input function $f(T)$. When (B3) is used to specify the constant in (B1), the result is

$$\bar{c}^f = \frac{A \bar{f}(p)}{1 - \frac{\lambda(p)}{P}} e^{\lambda(p)X} = \bar{f}(p) \bar{c}^\delta \quad (\text{B4})$$

where the superscript f denotes the general pulse input solution.

The Laplace-domain solutions are related to the solute breakthrough time moments by (26). Therefore

$$m_n^f = (-1)^n \lim_{p \rightarrow 0} \left[\frac{d^n \bar{c}^f}{dp^n} \right] \quad (\text{B5})$$

The relation between \bar{c}^f and \bar{c}^δ given by (B4) and the general form of the chain rule given by Abramowitz and Stegun [1972, p. 12] will yield

$$\frac{d^n \bar{c}^f}{dp^n} = \frac{d^n}{dp^n} (\bar{f} \bar{c}^\delta) = \frac{d^n \bar{f}}{dp^n} \bar{c}^\delta + \sum_{r=1}^{n-1} \binom{n}{r} \frac{d^{n-r} \bar{f}}{dp^{n-r}} \frac{d^r \bar{c}^\delta}{dp^r} + \bar{f} \frac{d^n \bar{c}^\delta}{dp^n} \quad (\text{B6})$$

where $\binom{n}{r}$ is the binomial coefficient defined as $n!/[r!(n-r)!]$. Substitution of (B6) into (B4) will yield after some algebraic

manipulation

$$m_n^f = \sum_{r=0}^n \binom{n}{r} v_{n-r} m_r^{\delta} \quad (B7)$$

where v_n denotes the n th absolute moment of the input function $f(T)$,

$$v_n = \int_0^{\infty} T^n f(T) dT = (-1)^n \lim_{p \rightarrow 0} \left[\frac{d^n f}{dp^n} \right] \quad (B8)$$

Because of the mass balance condition (57) on $f(T)$, $m_0^f = m_0^{\delta}$. Dividing (B7) by m_0 will give the following relationship between the normalized moments for the general pulse and Dirac input solutions:

$$\mu_n^f = \sum_{r=0}^n \binom{n}{r} v_{n-r} \mu_r^{\delta} \quad (B9)$$

Equation (B9) can be used in conjunction with the well-known relationship between absolute and central moments [Kendall and Stuart, 1977, p. 58]

$$\mu_n = \sum_{r=0}^n \binom{n}{r} \mu_{n-r} (\mu_1)^r$$

to give the following useful expressions for the first three moments:

$$\mu_1^f = \mu_1^{\delta} + v_1 \quad (B10)$$

$$\mu_2^f = \mu_2^{\delta} + v_2 \quad (B11)$$

$$\mu_3^f = \mu_3^{\delta} + v_3 \quad (B12)$$

where v_n is the n th central moment of $f(T)$.

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