

Solute transport with multiprocess nonequilibrium: a semi-analytical solution approach

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Abstract

A semi-analytical solution for the simulation of one-dimensional subsurface solute transport incorporating multiple nonequilibrium processes is presented. The solution is based on the theory developed by Brusseau et al. (1992) [Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1992. Modeling solute transport influenced by multiprocess nonequilibrium and transformation reactions. *Water Resources Research* 28 (1), 175-182.] which is a generalized combination of two-site and two-region model. In addition to developing a semi-analytical complement to their numerical solution, we extend the range of boundary and initial conditions considered. The semi-analytical solution can represent domains of both finite and semi-infinite extent and accommodates nonzero initial concentrations. The solution is derived in Laplace space and final results are obtained using an accurate and robust numerical inversion algorithm. The solution is particularly well suited for interpreting experimental results obtained under controlled laboratory conditions. Identification of the input parameters for the solution is examined by simulating a column experiment by van Genuchten (1974) [van Genuchten, M., 1974. *Mass Transfer Studies in Sorbing Porous Media*. PhD thesis, New Mexico State University, Las Cruces, NM.]. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mathematical models of solute transport are important tools for solving problems involving groundwater contamination. Potential applications of models include planning of site investigations, risk assessment, and design of remedial actions. These models must be capable of representing the most significant processes affecting the transport of solutes. There is evidence to suggest that models based on assumptions of ideal behavior ignore fundamental characteristics of the transport of solutes (reviews are presented by Bouchard et al., 1988 and Brusseau and Rao, 1989a,c).

The transport of sorbing solutes is generally modeled with an idealized model, in which the porous is represented as an interconnected continuum, and sorption is represented as an equilibrium process (instantaneous and reversible) with a linear isotherm. For a pulse input, this approach predicts symmetrical, bell-shaped breakthrough curves. Departures from this ideal behavior have been observed at scales of investigation ranging from column experiments to field-scale tests. Two examples of nonideality are shown in Fig. 1. Fig. 1a plots results from a column experiment with the herbicide 2,4,5-D (2,4,5-trichlorophenoxyacetic acid) reported by van Genuchten et al. (1977). Fig. 1b, taken from Goltz and Roberts (1986a), illustrates concentrations of tetrachloroethene observed during the Stanford–Waterloo natural-gradient tracer test. Of particular importance are the long tails of the breakthrough curves. If tailing is not considered, then the ability to provide quantitative answers to basic questions is severely compromised. For example, in the context of pump-and-treat remediation of contaminated sites, the duration of pumping and the volume of treated water cannot be estimated reliably.

Two general mechanisms have been offered as explanations for nonideal behavior. The first mechanism is adapted from the dual porosity hypothesis and is designated

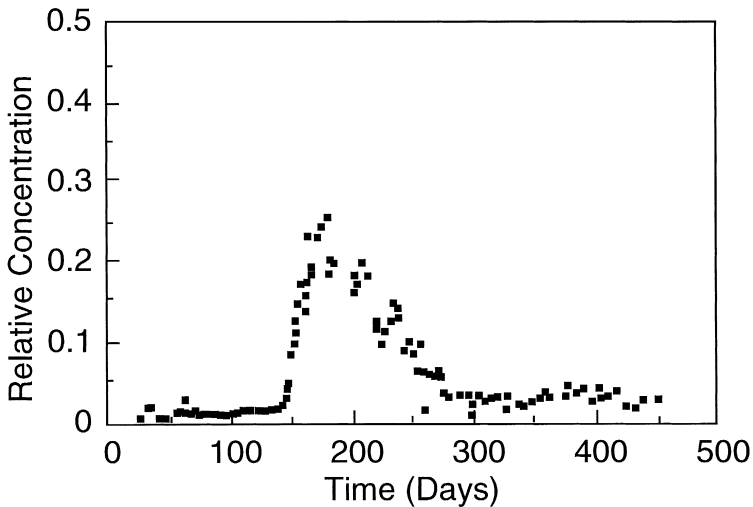


Fig. 1. Evidence of transport nonequilibrium from a field-scale experiment (Goltz and Roberts, 1986a,b).

physical nonequilibrium (PNE). Originally developed to represent flow in densely fractured porous media, the dual porosity hypothesis idealizes the porous medium as two interacting continua. In the first continuum (the mobile region), the pore water is relatively mobile, while in the second (the immobile region), advection is minimal (Coats and Smith, 1964). Solute transport in a dual porosity medium is characterized by early breakthrough resulting from rapid advective transport in the mobile region and tailing resulting from the slow diffusive mass transfer between the mobile and immobile regions.

Different models for dual porosity have been developed based on assumptions about the geometry of the mobile and immobile regions. Geometrical models conceive of the immobile region as an idealized assemblage of simple elements, for example, as uniform slabs and spheres (e.g., Huyakorn et al., 1983). An alternative approach is to represent the diffusive flux between the mobile and immobile regions by a first-order mass transfer reaction. The first-order mass transfer approach has been applied to cases of aggregated porous media (van Genuchten and Wierenga, 1977; van Genuchten et al., 1977), and discrete layering (Brusseau, 1991). The first-order approach has also been applied to simulate transport in heterogeneous aquifers (Brusseau and Rao, 1989b; Brusseau and Srivastava, 1997). In this context, the approach is purely phenomenological and the mass transfer coefficient becomes merely a fitting parameter.

PNE affects the transport of both sorbing and nonsorbing solutes and is commonly associated with aggregated and fractured porous media. However, tailing has also been observed in column studies with sorbing organic solutes in uniform, granular porous media (e.g., Liu et al., 1991). Therefore, a second mechanism has been proposed to explain nonideal behavior of organics. This second mechanism is designated sorption nonequilibrium (SNE). SNE represents the combined effects of intrasorbent (intraorganic or intramineral) diffusion and rate-limited interactions between the solute and sorbent. In the two-site conceptualization, sorption is assumed to occur at two sites: at the first site, sorption is an equilibrium process; at the second site, sorption is a rate-limited process. The rate-limiting sorption reaction is represented as a first-order reaction.

Many analytical solutions based on the mobile-immobile conceptualization, referred to as two-region models, have been developed. Examples included those of van Genuchten and Wierenga (1976) and Goltz and Roberts (1986b). Carnahan and Remer (1984) presented an analytical solution incorporating rate-limited sorption. Analytical solutions based on the two-site model have also been developed by Cameron and Klute (1977) and van Genuchten and Wagenet (1989). It has been long recognized that two-region and two-site models are mathematically identical. Several studies used this identity to develop analytical solutions to handle either physical or chemical nonequilibrium (i.e., two-site or two-region models) (e.g., Leij et al., 1993; Toride et al., 1993; Leij and van Genuchten, 2000). However, none of the existing solutions can be used to handle both nonequilibrium processes simultaneously.

Brusseau et al. (1989) formulated a model that incorporates both physical and sorption nonequilibria, which they called the multiprocess nonequilibrium (MPNE) model. Brusseau et al. (1992) extended the model to consider transformation reactions represented as first-order decay processes. The model integrates the two-region and

two-site conceptualizations. The mobile and immobile regions are each subdivided into three compartments. The first compartment in each region is the dissolved phase and the second and third compartments constitute the two sites of the sorbed phase. The sorption sites are split into a fraction where sorption occurs instantaneously, and a remaining fraction where sorption follows first-order kinetics. Transport between the mobile and immobile regions is modeled with a first-order mass transfer approach.

Several numerical models implementing the MPNE model have been developed. Brusseau et al. (1992) used a one-dimensional finite difference solution to simulate column experiments. Sudicky (personal communication, 1989) developed the first two-dimensional finite element solution to the MPNE equations. The solution is based on the Laplace Transform Galerkin (LTG) technique presented in Sudicky (1989, 1990) and was used by Brusseau et al. (1989) to assess the relative contributions of chemical sorption kinetics, intraparticle diffusion and geologic heterogeneity on plume evolution. Therrien et al. (1990) extended the LTG solution to three dimensions and applied their model to the interpretation of forced-gradient tracer tests in heterogeneous sand aquifers. Recently, Zhang and Brusseau (1999) have published an important field-scale application of the MPNE model with a three-dimensional numerical solution based on the modified method of characteristics.

In this paper, we present an analytical Laplace transform solution for one-dimensional transport with MPNE. Exact analytical or semi-analytical solutions generally can be derived only for problems involving homogeneous media and simple boundary conditions. In light of these restrictions, and the existence of general numerical solutions, the obvious question is: why develop an analytical solution for MPNE? The first answer is that these sophisticated numerical solutions demand verification. Second, there exists a need for simple solutions that can be used as screening tools, particularly for preliminary modeling in the absence of data. Finally, analytical solutions are ideally suited for the interpretation of experimental results obtained under controlled laboratory conditions. For this application, their freedom from spatial and temporal discretization requirements is a significant advantage over numerical solutions.

The solution is derived using the Laplace transform technique, with the final results obtained by numerical inversion of the transformed solution. Special attention is directed towards implementing the solution in a code that is robust and capable of predicting concentrations over a wide range of environmental interest. The solution is verified using the results of a numerical simulation of a column experiment. The identifiability of input parameters for laboratory-scale applications is examined by simulating van Genuchten (1974) experiments 3–5.

2. Mathematical formulation

In this section, we develop the governing equations of the MPNE model in order to clarify each equilibrium/nonequilibrium process which constitute the model. This level of detail in the mathematical formulation is typically missing from the literatures on two-region and/or two-site models (e.g., Brusseau et al., 1989).

2.1. Assumptions

The key assumptions of the MPNE model are summarized below. (1) The domain is represented as a dual porosity continuum. Mass transfer between the mobile and immobile regions is modeled as a first-order mass transfer reaction. (2) Sorption occurs at both equilibrium and rate-limited sites. At the equilibrium sites, sorption is instantaneous and reversible and is governed by a linear isotherm. At the rate-limited sites, sorption is represented as a first-order reaction. The mobile and immobile regions are characterized by separate sorption properties. (3) Transformation reactions are modeled as first-order decay processes. If microbially-mediated reactions are represented using this approach, then it is tacitly assumed that they are not limited by substrate availability (e.g., oxygen is in unlimited supply) and that contaminant concentrations are relatively low (Criddle et al., 1991). For maximum generality, the dissolved and sorbed phases in the mobile and immobile regions are assigned separate decay rates.

Several additional assumptions are required for a tractable one-dimensional analytical treatment:

1. The material properties are spatially uniform and temporally constant.
2. The Darcy flux is steady, one-dimensional, and spatially uniform.
3. Longitudinal dispersion is assumed to be a Fickian process, characterized by a constant dispersion coefficient. Dispersion in the transverse directions is neglected.
4. The initial concentrations in the domain are uniform. For maximum generality, the initial concentrations are specified separately for the dissolved and sorbed phases.

2.2. Governing equations

The MPNE model is cast in terms of six concentrations: one dissolved phase and two sorbed phase concentrations for each of the mobile and immobile regions. In the following development, use is made of mass balance equations and constitutive relations to derive the six equations, which comprise the MPNE model.

2.2.1. Mobile region

Within the mobile region, the MPNE model accounts for advective–dispersive transport, mobile–immobile mass transfer, equilibrium and rate-limited sorption and first-order transformation reactions. The statement of mass conservation for the dissolved phase in the mobile region is written as:

$$\frac{\partial(\theta_m C_m)}{\partial t} + \frac{\partial(f\rho S_m)}{\partial t} = -\frac{\partial J_m}{\partial x} - G_{\lambda_m} - G_{\lambda_{s_m}} - G_{im} \quad (1)$$

The terms appearing in this and all subsequent equations are defined in the Notation. The left-hand side of the mass balance equation represents the time rate of change of mass in the dissolved and sorbed phases in the mobile region. In this expression, the term f designates the mass fraction of sorbent that is accessible to the dissolved phase in

the mobile region. Solute in the sorbed phase is partitioned between the equilibrium and rate-limited sorption sites:

$$S_m = S_{m1} + S_{m2} \quad (2)$$

The first term on the right-hand side in Eq. (1) is the advective–dispersive mass flux in the dissolved phase and is defined as:

$$J_m = -\theta_m D \frac{\partial C_m}{\partial x} + q C_m \quad (3)$$

The second and third terms on the right-hand side, G_{λ_m} and $G_{\lambda_{S_m}}$, are sinks representing first-order transformation reactions in the dissolved and sorbed phases. The first-order transformation sink terms are written as:

$$G_{\lambda_m} = \theta_m \lambda_m C_m \quad (4)$$

$$G_{\lambda_{S_m}} = f\rho(\lambda_{S_{m1}} S_{m1} + \lambda_{S_{m2}} S_{m2}) \quad (5)$$

For the first-order mass transfer model, the sink term representing mobile–immobile interaction is expressed as:

$$G_{im} = \alpha(C_m - C_{im}) \quad (6)$$

Assembling all of the terms in the original mass balance, Eq. (1) yields:

$$\begin{aligned} \frac{\partial(\theta_m C_m)}{\partial t} + f\rho \frac{\partial S_{m1}}{\partial t} + f\rho \frac{\partial S_{m2}}{\partial t} = & \frac{\partial}{\partial x} \left(\theta_m D \frac{\partial C_m}{\partial x} \right) - \frac{\partial}{\partial x} (q C_m) - \theta_m \lambda_m C_m \\ & - f\rho(\lambda_{S_{m1}} S_{m1} + \lambda_{S_{m2}} S_{m2}) - \alpha(C_m - C_{im}) \end{aligned} \quad (7)$$

The sorbed phase concentration at the instantaneous sorption sites is defined in terms of the following equilibrium constitutive relation:

$$S_{m1} = F_m K_m C_m \quad (8)$$

In this relation, F_m represents the mass fraction of sorption sites in the mobile region where sorption is instantaneous. The sorbed phase concentration at the rate-limited sites is defined in terms of a mass balance equation:

$$\frac{\partial S_{m2}}{\partial t} = k_{m2}[(1 - F_m) K_m C_m - S_{m2}] - \lambda_{S_{m2}} S_{m2} \quad (9)$$

Substituting for the sorbed phase concentrations and invoking the assumption of constant material properties yields the final form of the transport equation for the mobile region:

$$\begin{aligned} (\theta_m + f\rho F_m K_m) \frac{\partial C_m}{\partial t} + (\theta_m \lambda_m + f\rho \lambda_{S_{m1}} F_m K_m) C_m + \alpha(C_m - C_{im}) \\ + f\rho k_{m2}[(1 - F_m) K_m C_m - S_{m2}] = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \end{aligned} \quad (10)$$

2.2.2. Immobile region

The governing equations for the immobile region are analogous to those derived for the mobile region, with the exception that advection and dispersion are not considered. The statement of mass conservation for the immobile region is written as:

$$\frac{\partial(\theta_{im} C_{im})}{\partial t} + \frac{\partial((1-f)\rho S_{im})}{\partial t} = -G_{\lambda_{im}} - G_{\lambda_{s_{im}}} + G_{im} \quad (11)$$

The left-hand side of the mass balance equation represents the time rate of change of mass in the dissolved and sorbed phases in the immobile region. In this expression, the term $(1-f)$ designates the mass fraction of sorbent that is accessible to the dissolved phase in the immobile region. Solute in the sorbed phase is partitioned between the equilibrium and rate-limited sorption sites:

$$S_{im} = S_{im1} + S_{im2} \quad (12)$$

The mobile-immobile mass transfer term, G_{im} , is defined by Eq. (6). The remaining components of the right-hand side sink term are analogous to those for the mobile region and are written as:

$$G_{\lambda_{im}} = \theta_{im} \lambda_{im} C_{im} \quad (13)$$

$$G_{\lambda_{s_{im}}} = (1-f)\rho(\lambda_{s_{im1}} S_{im1} + \lambda_{s_{im2}} S_{im2}) \quad (14)$$

The expressions for the sinks are similar to those presented for the mobile region, noting that the sign of the mobile-immobile mass transfer term is reversed.

Assembling all of the terms in the mass balance, Eq. (11) yields:

$$\begin{aligned} \frac{\partial(\theta_{im} C_{im})}{\partial t} + (1-f)\rho \frac{\partial S_{im1}}{\partial t} + (1-f)\rho \frac{\partial S_{im2}}{\partial t} \\ = -\theta_{im} \lambda_{im} C_{im} - (1-f)\rho(\lambda_{s_{im1}} S_{im1} + \lambda_{s_{im2}} S_{im2}) + \alpha(C_m - C_{im}) \end{aligned} \quad (15)$$

The sorbed phase concentrations at the instantaneous and rate-limited sorption sites are defined by:

$$S_{im1} = F_{im} K_{im} C_{im} \quad (16)$$

$$\frac{\partial S_{im2}}{\partial t} = k_{im2} [(1 - F_{im}) K_{im} C_{im} - S_{im2}] - \lambda_{s_{im2}} S_{im2} \quad (17)$$

In these relations, F_{im} represents the mass fraction of sorption sites in the immobile region where sorption is instantaneous.

Substituting for the sorbed phase concentrations and invoking the assumption of constant material properties yields the final form of the transport equation for the immobile region:

$$\begin{aligned} (\theta_{im} + (1-f)\rho F_{im} K_{im}) \frac{\partial C_{im}}{\partial t} + (\theta_{im} \lambda_{im} + (1-f)\rho \lambda_{s_{im1}} F_{im} K_{im}) C_{im} \\ + (1-f)k_{im2} \rho [(1 - F_{im}) K_{im} C_{im} - S_{im2}] = \alpha(C_m - C_{im}) \end{aligned} \quad (18)$$

The governing equations presented here differ from Eqs. (4) and (5) of Brusseau et al. (1992). In particular, their equations are missing decay terms for the equilibrium sorbed

phases. The equations defining the concentrations in the equilibrium sorbed phases are more correctly interpreted here as constitutive relations rather than mass balance equations.

2.3. Initial and boundary conditions

2.3.1. Initial conditions

The model of Brusseau et al. (1992) assumes that the domain is initially devoid of contaminants. The initial conditions considered by our analytical solution are somewhat more general. It is assumed that the domain is uniformly contaminated and that the initial concentrations in each of the compartments are specified independently:

$$C_m(x,0) = C_m^0 \quad (19a)$$

$$C_{im}(x,0) = C_{im}^0 \quad (19b)$$

$$S_{m2}(0) = S_{m2}^0 \quad (19c)$$

$$S_{im2}(0) = S_{im2}^0 \quad (19d)$$

If the initial condition of the domain is such that $C_m^0 \neq 0$, and has existed as such for a long period of time, then the following initial concentrations may be assigned:

$$C_m(x,0) = C_m^0 \quad (20a)$$

$$C_{im}(x,0) = C_m^0 \quad (20b)$$

$$S_{m2}(0) = K_m C_m^0 \quad (20c)$$

$$S_{im2}(0) = K_{im} C_m^0 \quad (20d)$$

2.3.2. Boundary conditions

Boundary conditions are required only for the dissolved phase in the mobile region. The model developed by Brusseau et al. (1992) considers a third-type inflow boundary condition. For the analytical solution, a “generalized” inflow boundary condition capable of representing either first or third-type conditions is used. Adopting the notation of Leij et al. (1991), the inflow boundary condition is expressed as:

$$qC_m(0,t) - \theta_m \delta D \frac{\partial}{\partial x} C_m(0,t) = qC_0[1 - H(t - t_0)] \quad (21)$$

where H is the Heaviside step function, designating a step input extending from time $= 0$ to t_0 . The reader should note that $\delta = 0$ and $\delta = 1$ specify first-type (Dirichlet) and third-type (Cauchy) boundary conditions, respectively.

The finite difference solution of Brusseau et al. (1992) is necessarily restricted to a finite domain. For analytical solutions, this restriction does not exist and both finite and semi-infinite domains are considered here. A finite domain is specified by the following outflow boundary condition:

$$\frac{\partial}{\partial x} C_m(L,t) = 0 \quad (22)$$

A semi-infinite domain is specified by the following outflow boundary condition:

$$C_m(\infty, t) = C_m^0 \exp(-\lambda_m t) \quad (23)$$

2.4. Analytical solutions in the Laplace domain

The final set of governing equations for the MPNE formulation comprises a set of four linear differential equations involving four unknown concentrations, i.e., C_m , C_{im} , S_{m2} and S_{im2} described in (Eqs. (10), (9), (18) and (17). The linearity of the governing equations is important because it offers the possibility of deriving analytical solutions using integral transform methods. The analytical solution is derived by straightforward application of the Laplace transform. The complete derivation of the solution is given in Neville (1992).

- Step (1): apply the Laplace transform with respect to time to each of the governing equations and to the boundary conditions.
- Step (2): solve the transformed governing equations for the rate-limited phases, expressing \bar{S}_{m2} and \bar{S}_{im2} in terms of \bar{C}_m and \bar{C}_{im} , respectively. The over-bars denote Laplace-transformed quantities.
- Step (3): solve the transformed mass transfer reaction by substituting for \bar{S}_{im2} , expressing \bar{C}_{im} in terms of \bar{C}_m only.
- Step (4): derive the final form of the transformed governing equation in terms of \bar{C}_m by substituting for \bar{C}_{im} and \bar{S}_{im2} . The transformed governing equation is a linear, second order ordinary differential equation.
- Step (5): derive the general solution for \bar{C}_m . For the case of zero initial concentration, the governing equation is homogeneous and the solution is obtained directly. For the case of nonzero initial concentration, the solution is derived as the sum of a complementary and a particular solution.
- Step (6): solve for the undetermined coefficients in the general solution by imposing the transformed boundary conditions. Separate solutions are developed separately for the cases of a semi-infinite and finite domain.

Semi-infinite domain

$$\bar{C}_m = \frac{q}{q - \theta_m \delta DH_1} \left(\frac{C_0}{p} [1 - \exp(-pt_0)] - \frac{\alpha G_1^0 + G_2^0}{B} \right) \exp(H_1 x) + \frac{\alpha G_1^0 + G_2^0}{B} \quad (24)$$

Finite domain

$$\bar{C}_m = \frac{D_2}{D_1} \exp(H_1 x) + \frac{D_3}{D_1} \exp(H_2 x) + \frac{\alpha G_1^0 + G_2^0}{B} \quad (25)$$

where

$$H_1 = \frac{q - \sqrt{q^2 + 4B\theta_m D}}{2\theta_m D} \tag{26a}$$

$$H_2 = \frac{q + \sqrt{q^2 + 4B\theta_m D}}{2\theta_m D} \tag{26b}$$

$$D_1 = H_2 (q - \theta_m \delta DH_1) \exp(H_2 L) - H_1 (q - \theta_m \delta DH_2) \exp(H_1 L) \tag{26c}$$

$$D_2 = \left(\frac{qC_0}{p} (1 - \exp(pt_0)) - q \frac{\alpha G_1^0 + G_2^0}{B} \right) H_2 \exp(H_2 L) \tag{26d}$$

$$D_3 = - \left(\frac{qC_0}{p} (1 - \exp(pt_0)) - q \frac{\alpha G_1^0 + G_2^0}{B} \right) H_1 \exp(H_1 L) \tag{26e}$$

$$B = \theta_m [\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4] \tag{26f}$$

$$\Gamma_1 = \left(1 + \frac{f\rho}{\theta_m} F_m K_m \right) p \tag{26g}$$

$$\Gamma_2 = \frac{1}{\theta_m} \left(f\rho(1 - F_m) K_m \frac{k_{m2}(p + \lambda_{S_{m2}})}{p + k_{m2} + \lambda_{S_{m2}}} \right) \tag{26h}$$

$$\Gamma_3 = \frac{1}{\theta_m} \left(\frac{\alpha\gamma - \alpha^2}{\gamma} \right) \tag{26i}$$

$$\Gamma_4 = \lambda_m + \frac{f\rho}{\theta_m} \lambda_{S_{m1}} F_m K_m \tag{26j}$$

$$\begin{aligned} \gamma = & p(\theta_{im} + \rho(1 - f)F_{im}K_{im}) + \theta_{im}\lambda_{im} + \rho(1 - f)F_{im}K_{im}\lambda_{S_{m1}} \\ & + \rho(1 - f)(1 - F_{im})K_{im}k_{im2} \frac{p + \lambda_{S_{m2}}}{p + \lambda_{S_{m2}} + k_{im2}} + \alpha \end{aligned} \tag{26k}$$

The terms G_1^0 and G_2^0 are associated with the initial conditions and are defined as:

$$\begin{aligned} G_1^0 = & \left[\frac{\rho(1 - f)k_{im2}}{p + \lambda_{S_{m2}} + k_{im2}} S_{im2}^0 + (\theta_{im} + \rho(1 - f)F_{im}K_{im})C_{im}^0 \right] \\ & \cdot \left[p(\theta_{im} + \rho(1 - f)F_{im}K_{im}) + \theta_{im}\lambda_{im} + \rho(1 - f)\lambda_{S_{m1}}F_{im}K_{im} \right. \\ & \left. + \rho(1 - f)(1 - F_{im})K_{im}k_{im2} \frac{p + \lambda_{S_{m2}}}{p + k_{im2} + \lambda_{S_{m2}}} + \alpha \right]^{-1} \end{aligned} \tag{27a}$$

$$G_2^0 = (\theta_m + \rho f F_m K_m) C_m^0 + \frac{\rho f k_{m2}}{p + k_{m2} + \lambda_{S_{m2}}} S_{m2}^0 \tag{27b}$$

2.4.1. Special cases

The advantage of the solution technique described here is its ability to represent a very general physical conceptualization, with flexible boundary and initial conditions. For example, when the SNE parameters, F_m and F_{im} , are set equal to 1.0 (i.e., all sites are equilibrium sites), the solution collapses to the two-region model. Similarly, when the mobile porosity is set equal to the total porosity (i.e., $\theta_m = \theta$) and the sorbent is specified to be completely accessible to the dissolved phase (i.e., $f = 1.0$), the solution reduces to the two-site model. Solutions for these special cases have been presented by van Genuchten and Wagenet (1989).

The solution developed here is also a relatively general model for equilibrium transport (specifying the porosity as entirely mobile and the sorption sites as all equilibrium-controlled). For a first-type (Dirichlet) inflow boundary condition ($\delta = 0$), the solution encompasses those of Ogata and Banks (1951), Lapidus and Amundson (1952), and Bear (1972, p. 630) for a semi-infinite domain, and Cleary and Adrian (1973) for a finite domain. For a third-type (Cauchy) inflow boundary condition ($\delta = 1$), the solution encompasses those of Bastian and Lapidus (1956), Lindstrom et al. (1967), and Gershon and Nir (1969) for a semi-infinite domain, and Brenner (1962) and Dankwerts (1953) for a finite domain.

3. Evaluation and verification

3.1. Evaluation

Final values of the solution are obtained by numerical inversion of the Laplace transform solution. The decision to numerically invert the transformed solution offers two immediate advantages: first, the difficult step of deriving an analytical inverse is eliminated; second, the transformed solution is generally easier to evaluate. This approach was introduced in the hydrogeologic literature by Moench and Ogata (1981), and is now used frequently to evaluate solutions (see for example Goltz and Oxley, 1991). The success of this approach hinges on the ability to carry out the inversion accurately. For diffusion-dominated problems, there are several algorithms that yield accurate results. Unfortunately, for advection-dominated problems involving sharp fronts, these inversion techniques generally fail, yielding spurious results or under/overflow problems.

The groundwater modeling group at the University of Waterloo has obtained excellent results using the inversion algorithm developed by de Hoog et al. (1982). This algorithm has been used for both numerical models (LTG method) and analytical solutions, and has been applied to a broad spectrum of conditions, ranging from pure diffusion to almost pure advection (Therrien et al., 1990; Sudicky and McLaren, 1992). The solution is implemented in a FORTRAN program. A copy of the code with documentation is available from the first author, free upon request.

3.2. Verification

The implemented solution has been tested extensively. We report here only the testing of the full MPNE formulation. Because no other analytical solutions based on the

Table 1
Parameters for experiments 1–4

Parameter	Value
Bulk density ρ	1.360 g/cm ³
Darcy flux q	5.11 cm/day
Dispersion coefficient D	3.673 cm ³ /day
Total water content θ	0.473
Proportion of mobile pore water ϕ	0.929
Fraction of mobile sorption sites f	0.929
Fraction of equilibrium sorption sites F_m	0.50
Fraction of equilibrium sorption sites F_{im}	0.50
Mass transfer coefficient α	0.075 day ⁻¹
Sorption coefficient K_m	0.429 cm ³ /g
Sorption coefficient K_{im}	0.416 cm ³ /g
Sorption rate constant k_{m2}	0.663 day ⁻¹
Sorption rate constant k_{im2}	0.663 day ⁻¹
Pulse period t_0	7.672 day
Column length L	30.0 cm

MPNE model have been reported, the solution developed here is compared against the results from a numerical solution.

The implementation of the MPNE formulation is verified by comparison with the Brusseau et al. (1989) simulations of the column experiments reported by van Genuchten

Table 2
Parameters for experiments 3–5

Parameter	Value
Bulk density ρ	1.222 g/cm ³
Total water content θ	0.456
Darcy flux q	3.975 cm/day
Pulse period t_0	9.653 day
Column length L	30.0 cm
Dispersion coefficient D	5.313 cm ³ /day
Proportion of mobile pore water ϕ	0.88
Mass transfer coefficient α	0.03 day ⁻¹
Sorption coefficient K_m	0.426 cm ³ /g
Sorption coefficient K_{im}	0.426 cm ³ /g
Sorption rate constant k_{m2}	0.66 day ⁻¹
Sorption rate constant k_{im2}	0.66 day ⁻¹
Fraction of equilibrium sorption sites F_m	0.50
Fraction of equilibrium sorption sites F_{im}	0.50
Fraction of mobile sorption sites f	0.88
Decay coefficient λ_n	0.058 day ⁻¹
Decay coefficient $\lambda_{S_{m1}}$	–
Decay coefficient $\lambda_{S_{m2}}$	–
Decay coefficient λ_{im}	–
Decay coefficient $\lambda_{S_{im1}}$	–
Decay coefficient $\lambda_{S_{im2}}$	–

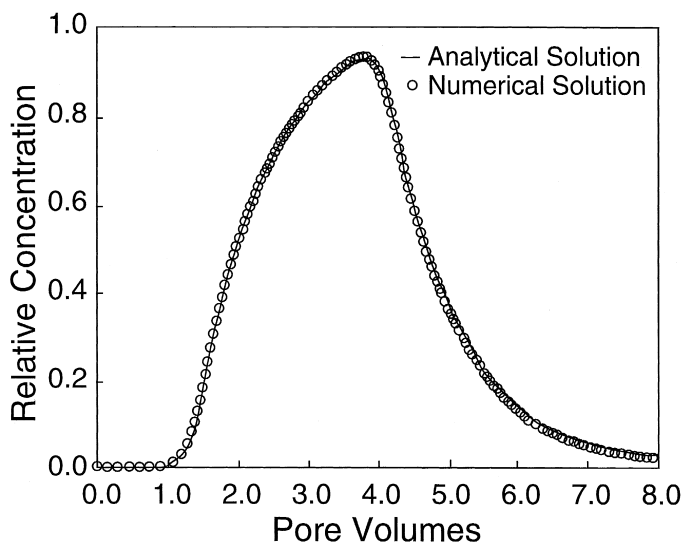


Fig. 2. Verification example: van Genuchten et al. (1977). Experiments 1–4.

et al. (1977). The column experiments were conducted to study the transport of the herbicide 2,4,5-D. The results presented by Brusseau et al. (1989) were obtained using a one-dimensional finite difference model incorporating Crank–Nicolson time-weighting. No information was provided about either the spatial or temporal discretizations used for their simulations, nor was there any indication of the criteria used to select these discretizations.

For the sake of brevity, only the comparison of the analytical and numerical solutions for the calibration of experiments 1–4 is presented here. The dimensionless parameters for the simulation are given in Brusseau et al. (1989, Fig. 6) but the corresponding dimensional parameter values are not reported. The dimensional parameters are listed here in Table 1. Some of the parameter values were obtained from van Genuchten et al. (1977, Tables 1 and 2). The remaining values were deduced from the values of the dimensionless parameters. The results of the analytical and numerical solutions are shown in Fig. 2. In Fig. 2, time is expressed as dimensionless pore volumes, defined as $T = qt/L\theta$.

4. Application of the MPNE model to van Genuchten (1974) experiments 3–5

In this section, we demonstrate the application of the MPNE model by re-visiting another of the van Genuchten and Wagenet (1989) experiments with 2,4,5-D, numbers 3–5. Brusseau et al. (1992) simulated this experiment with their numerical solution, but presented only a brief discussion of the identification of input parameters. We expand upon this discussion in order to clarify the interpretation of the input. The final parameter set is assembled in Table 2.

4.1. Input parameters

4.1.1. Basic data (ρ , θ , q , t_0 , L)

The basic data for the simulation are taken from van Genuchten (1974). These data correspond to the preliminary measurements required for any simulation.

4.1.2. Dispersion coefficient, PNE parameters (D , ϕ , α)

van Genuchten conducted column experiments with tritiated water to provide independent estimates of the dispersion coefficient and PNE parameters. Tritium sorbs relatively weakly, and its half-life of about 12 years is much longer than the duration of the column experiments. Therefore, for the purposes of this analysis, it is assumed to be a nonreactive tracer.

According to the conceptual model of MPNE, PNE affects both sorbing and nonsorbing solutes. Therefore, the tritium breakthrough data are interpreted using a two-region model. The conditions for experiments 3–5 are most similar to those reported for experiments 3–4 by van Genuchten and Wierenga (1977). From their analysis of the data, van Genuchten and Wierenga (1977) estimated a dispersion coefficient, D , of 5.7 cm²/day, a proportion of mobile pore water, ϕ equal to 0.88, and mass transfer coefficient, α of 0.10 day⁻¹. We assume that the dispersion coefficient is dominated by mechanical dispersion, so that the dispersion coefficient for experiments 3–5 can be estimated by scaling the dispersion coefficient with respect to the Darcy flux. The Darcy flux for experiments 3–4 is 4.20 cm/day while the flux for experiments 3–5 is 3.975 cm/day. Hence, the estimated dispersion coefficient for experiments 3–5 is 5.3 cm²/day.

A mass transfer coefficient for tritium was estimated from experiments 3–4. The mass transfer coefficient for 2,4,5-D is estimated by adjusting the fitted value for tritium according to the ratios of the free-solution diffusion coefficients (Brusseau et al., 1992).

$$\alpha = \alpha_{\text{exp. 3-4}} \frac{D_{2,4,5\text{-D}}^0}{D_{3\text{H}}^0}$$

where α and $\alpha_{\text{exp. 3-4}}$ are the mass transfer coefficients for 2,4,5-D and experiments 3–4, respectively, and $D_{2,4,5\text{-D}}^0$ and $D_{3\text{H}}^0$ are the free-solution diffusion coefficients for 2,4,5-D and 3H, respectively.

4.1.3. Sorption parameters (K , k , F , f)

van Genuchten et al. (1977) reported the results of batch sorption tests with 2,4,5-D. The sorption data were found to follow a nonlinear Freundlich isotherm. For an equilibrium porewater concentration C in units of $\mu\text{g}/\text{cm}^3$ and solid phase concentration S in units of $\mu\text{g}/\text{g}$, they obtained the mildly nonlinear relation.

$$S = 0.616C^{0.792}$$

The analytical approach developed for this study does not accommodate nonlinear solution. Hence, we follow the approach adopted by van Genuchten (1974) in using an

equivalent linearized sorption coefficient. For a porewater concentration ranging from 0 to 10 ($\mu\text{g}/\text{cm}^3$), the linearized sorption coefficient, K^1 , is defined by:

$$\int_0^{10} K^1 C dc = \int_0^{10} 0.616 C^{0.792} dC$$

Integrating both sides yields a linearized partitioning coefficient K^1 of $0.426 \text{ cm}^3/\text{g}$. For this simulation, it is assumed that the sorption coefficient is the same for the mobile and immobile regions, i.e., $K_m = K_{im} = K_p$.

The rate constant for nonequilibrium sorption is estimated by using a correlation with batch sorption coefficients presented by Brusseau and Rao (1992):

$$\log k_2 = -1.789 - 0.63 \log K_p$$

where k_2 is the kinetic desorption coefficient, and K_p is the partitioning (sorption) coefficient.

It is assumed that the partitioning (sorption) coefficient in this relation is given by the linearized coefficient K^1 . Using a value of K_p of 0.426, we calculate $k_2 = 0.66 \text{ day}^{-1}$. For this simulation, it is assumed that the mobile and immobile rate constants are the same, i.e., $k_{m2} = k_{im2}$.

The fractions of instantaneous sorption sites in the mobile and immobile regions are assigned the same assumed value, $F_m = F_{im} = 0.5$. It is also assumed that the proportion of sorption sites that are accessible to the solute in the mobile region is equal to the proportion of the pore water that is mobile, i.e., $f = \phi$.

4.1.4. Decay coefficients

A decay rate for the dissolved phase in the mobile region was estimated by Brusseau et al. (1992), $\lambda_m = 0.058 \text{ day}^{-1}$. It is assumed that decay only occurs in the dissolved phase in the mobile region.

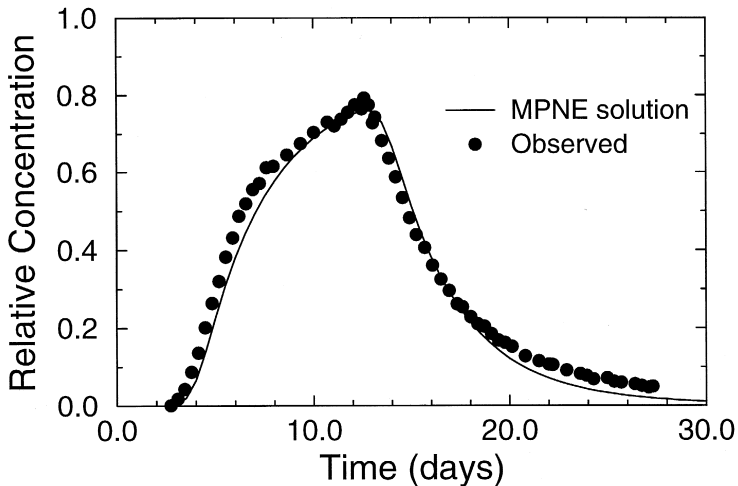


Fig. 3. Application example of the MPNE model for van Genuchten experiments 3–5.

4.2. Results

The observed breakthrough data and results obtained from the analytical solution are shown in Fig. 3.

5. Conclusions

In this paper, it has been demonstrated that the Laplace transform is an effective technique for developing analytical solutions for simulating nonidealities in solute transport. The solution derived here is based on the MPNE model developed by Brusseau et al. (1989, 1992) and is capable of representing a wider range of boundary and initial conditions than their numerical solution. The advantage of the Laplace transform technique is that it allows for straightforward derivation of analytical solutions that incorporate a very general physical conceptualization, with a broad range of boundary and initial conditions. The use of the algorithm of de Hoog et al. (1982) to numerically invert the Laplace-transformed solutions yields a code that is accurate and robust.

Quantitative analysis of field-scale processes is only possible if laboratory data are available to estimate some of the MPNE parameters. The real utility of the solution will be in the analysis of data obtained under controlled laboratory conditions. The analytical solution can be readily incorporated as a subroutine in automated parameter estimation codes. For this application, its freedom from discretization and time-stepping requirements represents a significant advantage over numerical models.

Notation

C_m	concentration in mobile region dissolved phase [ML^{-3}]
C_{im}	concentration in immobile region dissolved phase [ML^{-3}]
S_{m1}	concentration at instantaneous sorption sites in mobile region [MM^{-1}]
S_{m2}	concentration at rate-limited sorption sites in mobile region [MM^{-1}]
S_{im1}	concentration at instantaneous sorption sites in immobile region [MM^{-1}]
S_{im2}	concentration at rate-limited sorption sites in immobile region [MM^{-1}]
t	time elapsed since beginning of solute release [T]
p	Laplace transformed variable for time [T^{-1}]
x	distance from inflow boundary [L]
L	length of the domain for finite case [L]
ρ	bulk density of porous medium [ML^{-3}]
q	Darcy flux [LT^{-1}]
D	hydrodynamic dispersion coefficient [L^2T^{-1}]
θ	total water content [-]
ϕ	proportion of pore water that is mobile [-] $\phi = \theta_m/\theta$
θ_m	mobile water content [-] $\theta_m = \phi\theta$
θ_{im}	immobile water content [-] $\theta_{im} = (1 - \phi)\theta$
f	mass fraction of sorbent in contact with the mobile region dissolved phase [-]
α	first-order mass transfer coefficient [T^{-1}]
F_m	and mobile region fraction of instantaneous sorption sites [-]

F_{im}	immobile region fraction of instantaneous sorption sites [-]
K_m	mobile region equilibrium sorption coefficient [L^3M^{-1}]
K_{im}	immobile region equilibrium sorption coefficient [L^3M^{-1}]
k_{m2}	mobile region first-order kinetic desorption coefficient [T^{-1}]
k_{im2}	immobile region first-order kinetic desorption coefficient [T^{-1}]
t_0	duration of the finite-duration source [T]
λ_m	mobile region dissolved phase first-order decay rate [T^{-1}]
$\lambda_{S_{m1}}$	mobile region instantaneous sorption sites first-order decay coefficient [T^{-1}]
$\lambda_{S_{m2}}$	mobile region rate-limited sorption sites first-order decay rate [T^{-1}]
λ_{im}	immobile region dissolved phase first-order decay rate [T^{-1}]
$\lambda_{S_{im1}}$	immobile region instantaneous sorption sites first-order decay rate [T^{-1}]
$\lambda_{S_{im2}}$	immobile region rate-limited sorption sites first-order decay rate [T^{-1}]
C_0	solute concentration in inflow reservoir [ML^{-3}]
δ	inflow boundary coefficient: = 0 Type 1 inflow boundary condition, = 1 Type 3 inflow boundary condition

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