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# An analytical model for nonlinear adsorptive transport through layered soils

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**Abstract.** Solute transport with nonlinear adsorption occurs in many situations involving inorganic chemical and metal contamination in soil and groundwater systems. The resulting isotherms can be highly nonlinear, and numerical solutions of the transport equation can encounter severe convergence difficulties. An analytical solution is developed for simulating one-dimensional transport in the layered soil column with nonlinear adsorption effects. The analytical solution is an exact solution for nondispersive transport and becomes an approximate one when dispersion effects are included. The accuracy of the solution has been examined using a numerical model under advection-dominated conditions. The derived analytical solution can be used for any form of nonlinear sorption isotherms given as closed-form functions, or tabulated data, with a general time-dependent source boundary condition. The heterogeneity of soils is handled by treating the soil column as a layered system. The resulting analytical model is suitable for estimating the leaching potential of metals or other solutes in the subsurface and for determining travel times of contaminants. Our analysis shows that the shape and nonlinearity of the sorption isotherm may have a controlling influence on transport behavior. Evaluation and application examples are provided to demonstrate applicability of the solution to solute and metal transport with both functional and tabular nonlinear isotherms.

## Introduction

Solute transport in porous media has been studied theoretically and experimentally in the literature. A mathematical model is commonly used to describe the controlling transport processes including advection, diffusion and dispersion, adsorption, and degradation. The mathematical description of solute movement generally results in partial differential equations to be solved analytically or numerically. Analytical solutions have contributed significantly to our knowledge of this subject [*van Genuchten and Alves*, 1982; *Javandel et al*., 1984]. Analytical solutions, when available, provide a better insight into the physics behind the transport phenomena and are computationally efficient and simple to use. However, analytical approaches are for the most part limited to situations of simple geometry domains, linear governing equations, and uniform and homogeneous systems.

The state of the art in modeling of subsurface migration of contaminants in porous media has advanced considerably since the 1960s [*Istok*, 1989; *Huyakorn and Pinder*, 1983; *Sudicky and Huyakorn*, 1991]. Along with efficient numerical methods and rapidly updated computer hardware a large number of numerical models have been developed and applied to complex field problems. However, the numerical technique cannot replace the analytical approaches completely, since numerical methods themselves (1) need verification against analytical solutions because of discretization errors and convergence and stability problems that may be especially troublesome for advection-dominated and nonlinear adsorption processes and (2) are intense in computational demand when modeling a heterogeneous porous medium system with uncertainties in physical properties and distributions using stochastic approaches.

The analytical approaches recently have been used to study nonlinear adsorptive transport in porous media. However, the adsorption functions in these studies are not general but limited to the Freundlich isotherm [*van der Zee and van Riemsdijk*, 1987], to the Langmuir equation [*van der Zee*, 1990a, b], or to the Langmuir-Freundlich type [*Berglund and Cvetkovic*, 1996]. An exact solution was obtained in a recent study [*Manoranjan and Stauffer*, 1996] for contaminant transport through the uniform soil column using the Langmuir sorption relation. Natural subsurface soils are heterogeneous and, in many cases, may be approximated as a layered system. Few analytical studies can be found in the literature which deal with nonlinear transport in heterogeneous or layered soils. *Bosma and van der Zee* [1992] conducted such a study and provided an approximate analytical solution to the problem of transport in a two-layered soil column. However, only one of the two layers adsorbs nonlinearly, and its behavior is described using the Freundlich isotherm.

In this paper we derive an analytical solution for nonlinear adsorptive transport through a heterogeneous soil column. The nonlinear adsorption functions can be defined as either a closed-form function or a tabulated isotherm. The soil column is represented using a number of layers with different transport properties and is subject to a general time-dependent concen-

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tration boundary condition at the inlet. The accuracy of the analytical solution has been examined by comparison with a numerical model, and excellent agreement has been obtained between the analytical and numerical solutions. For demonstrative purposes the solution has been used to predict both spatial distributions and breakthrough curves of concentration for a two-layered soil column. Also, a metal transport analysis is presented using a tabulated isotherm. The new analytical solution will find its applications in obtaining physical insight into transport phenomena of nonlinear adsorbing solute through a layered soil system under advection-dominated conditions.

## Mathematical Formulation and Solution

The mathematical formulation for solute transport in a one-dimensional soil column has been discussed extensively in the literature [*van Genuchten and Alves*, 1982; *Bolt*, 1979; Bosma and van der Zee, 1992]. In this work, nonlinear adsorptive transport of a chemical species through a heterogeneous soil column is considered. The physical domain is a composite, layered soil column, consisting of $n$ layers, representing the unsaturated zone of a groundwater system.

The governing equation for transport in soil layer $j$ is given by

$$\frac{\partial}{\partial z}\left(D_j \frac{\partial c}{\partial z}\right) - v_j \frac{\partial c}{\partial z} = \frac{\partial}{\partial t}(c + f_j(c)) \qquad j = 1, 2, \cdots, n \tag{1}$$

where $z$ is a vertical coordinate with the origin at the soil surface, $c$ is the species concentration in the aqueous phase $(M/L^3)$, $D_j$ is the apparent dispersion coefficient $(L^2/T)$ in layer $j$, $v_j$ is the pore fluid velocity in layer $j$, and $f_j(c)$ $(M/L^3)$ is a nonlinear function representing the adsorption isotherm in layer $j$.

The hydrodynamic dispersion coefficient $D_j$ in (1) is defined as

$$D_j = \alpha_{Lj} v_j + D_j^* \qquad j = 1, 2, \cdots, n \tag{2}$$

where $\alpha_{Lj}$ is the vertical longitudinal dispersivity $(L)$, and $D_j^*$ is the effective molecular diffusion coefficient $(L^2/T)$. The pore velocity is evaluated as

$$v_j = V/\theta_j \qquad j = 1, 2, \cdots, n \tag{3}$$

where $V$ is the steady state Darcy velocity, which is assumed to be constant and equal to the rate of infiltration across all the layers, and $\theta_j$ is the water content, constant in layer $j$.

The nonlinear effect is expressed in terms of the adsorption function $f_j(c)$. If, for instance, the Freundlich adsorption isotherm is used for layer $j$ [*van der Zee*, 1990b], $f_j(c)$ may be expressed as

$$f_j(c) = \frac{\rho_{bj}}{\theta_j} K_j c^{\eta} \qquad j = 1, 2, \cdots, n \tag{4}$$

where $K_j$ $(L^{3\eta}/M^{\eta})$ and $\eta$ (dimensionless) are referred to as the coefficient and exponent of the Freundlich isotherm, respectively, and $\rho_{bj}$ is the bulk density of soil material in layer $j$. Although $\eta$ may also vary from layer to layer, we assume that it is constant for the sake of convenience in presenting the following derivation. Differentiating (4) with respect to $c$, one obtains

$$df_j/dc = f_j'(c) = \frac{\rho_{bj}}{\theta_j} K_j \eta c^{\eta - 1} \tag{5a}$$

which may be expressed in the form

$$f_j'(c) = \frac{\rho_{bj}}{\theta_j}(K_{dj}^*) \tag{5b}$$

where $K_{dj}^* = K_j \eta c^{\eta - 1}$ is referred to as an effective equilibrium partition coefficient between the solid and aqueous phases. By definition, $K_{dj}^*$ $(L^3/M)$ is the ratio of adsorbed concentration to dissolved concentration for layer $j$.

An exact analytical solution to (1) in general form is intractable because of the nonlinear adsorption term. Our objective is to investigate solute transport phenomena with nonlinear adsorption under time-dependent source conditions using approximate analytical techniques. The initial and boundary conditions for the one-dimensional transport problem may be expressed as follows:

Initial condition

$$c(z, t = 0) = c_i \qquad z > 0 \tag{6}$$

Boundary condition

$$c(z = 0, t) = c_0(t) \qquad c_0 \neq c_i \tag{7}$$

For pulse injection the surface boundary condition takes the form

$$c(z = 0, t) = \begin{cases} c_0 & t \leq T_p \\ 0 & t > T_p \end{cases} \tag{8}$$

where $c_i$ is the initial solute concentration, $c_0(t)$ is the source concentration as a function of time, and $T_p$ is the time period (pulse duration) during which a constant concentration source is applied at the surface boundary.

As mentioned earlier, there is no exact analytical solution available in the literature for (1) with the conditions (5)–(7). In order to solve the problem, some approximations are necessary. If the solute transport is advection dominated, we may ignore the effects of the dispersion term in (1). Consequently, the transport equation in layer $j$ can be written as

$$v_j \frac{\partial c}{\partial z} + [1 + f_j'(c)] \frac{\partial c}{\partial t} = 0 \tag{9}$$

Equation (9) is a quasi-linear first-order differential equation, describing the travel of concentrations (waves) at different characteristic speeds as given by [*Hildebrand*, 1976]

$$\left(\frac{dz}{dt}\right)_c = \frac{v_j}{1 + f_j'(c)} \tag{10}$$

The complete solution of the problem can be derived from (10), subject to the initial and boundary conditions (6)–(8).

Equation (10) indicates that the wave-traveling speed $[dz/dt]_c$ for a particular concentration $c$ is constant and dependent on the pore velocity $v_j$ as well as the adsorption function $f_j(c)$. Upon integration of (10) for a particular concentration $c$ the penetration depth or coordinate position $z_c$ of the concentration is obtained at any time $t$ $(t > t_s)$,

$$\int_{z_s}^{z_c} dz = \int_{t_s}^{t} \frac{v_j\, dt}{1 + f_j'(c)} \tag{11a}$$

which yields

$$z_c = \frac{v_j(t - t_s)}{1 + f_j'(c)} + z_s \tag{11b}$$

if the concentration wave $c$ starts traveling from $z = z_s$ at $t = t_s$.

The above analytical solution results from a direct application of chromatographic transport theory to the solute transport problem [*Hirasaki*, 1981; *Helfferich*, 1981]. As in the *Buckley and Leverett* [1942] theory for multiphase flow, a shock (abrupt front) may develop during the concentration propagation. The occurrence of the abrupt concentration front depends on the initial and boundary conditions [*van der Zee*, 1990b]. In order to use the above frontal advance approach (11b) to describe solute transport with nonlinear adsorption effects, one has to recognize the conditions under which a discontinuous (shock) front will develop; otherwise, a nonphysical solution may be derived.

There are two common situations that may lead to the occurrence of shock front in the first soil layer. If the initial concentration $c_i$ is constant and the incoming fluid at $z = 0$ has a different concentration of $c_o$, a shock front will develop under the following conditions [*van der Zee*, 1990b]:

Type 1 conditions

$$\begin{gathered} c_o > c_i \\ df_1(c)/dc > 0 \\ d^2f_1(c)/dc^2 < 0 \end{gathered} \tag{12}$$

Type 2 conditions

$$\begin{gathered} c_o < c_i \\ df_1(c)/dc > 0 \\ d^2f_1(c)/dc^2 > 0 \end{gathered} \tag{13}$$

The two types of conditions represented by (12) and (13) can be better understood physically using the Freundlich adsorption isotherm as an example. For a case involving continuous release of solute with concentration $c_o$ at the source and uniform initial (background) concentration $c_i$ within the system, the following conditions are satisfied:

$$\begin{gathered} c_o > c_i \\ \frac{df_1(c)}{dc} = \frac{\rho_{b_1}K_1}{\theta_1}\,\eta c^{\eta-1} > 0 \\ \frac{d^2f_1(c)}{dc^2} = \frac{\rho_{b_1}K_1}{\theta_1}\,\eta(\eta - 1)c^{\eta-2} < 0 \\ 0 < \eta < 1 \end{gathered} \tag{14}$$

which corresponds to type 1 conditions (12). Consequently, a shock front will exist during the transport process. Using (10), the traveling velocity is obtained as

$$\begin{gathered} \left(\frac{dz}{dt}\right)_c = \frac{v_1}{1 + \dfrac{\rho_{b_1}K_1}{\theta_1}\,\eta c^{\eta-1}} \\ 0 < \eta < 1, \quad z < d_1. \end{gathered} \tag{15}$$

For $c \to 0$, $c^{\eta-1} \to \infty$ and

$$(dz/dt)_c \to 0 \tag{16}$$

For $c \to \infty$, $c^{\eta-1} \to 0$ and

$$(dz/dt)_c \to v_1 \tag{17}$$

From (16) and (17), it may be deduced that the higher the concentration, the higher the traveling velocity. This situation is physically unattainable leading to the occurrence of a discontinuous (shock) front. The shock front velocity is given by

$$\left(\frac{\Delta z}{\Delta t}\right)_{\Delta c} = \frac{v_1}{1 + \dfrac{\Delta f_1(c)}{\Delta c}} \tag{18}$$

where $\Delta c = c_0 - c_i$ represents the concentration jump across the front. The penetration depth of the type 1 front is determined from

$$z_f = \frac{\theta_1 v_1 t(c_o - c_i)}{\theta_1(c_o - c_i) + \rho_{b_1}K_1(c_o^\eta - c_i^\eta)} \qquad z_f < d_1 \tag{19}$$

For a pulse release of solute and the same range of the Freundlich exponential parameter $0 < \eta < 1$ the conditions represented by (14) will not be satisfied at the entrance boundary $z = 0$ when $t > T_p$, the pulse duration. Consequently, adsorption according to the Freundlich isotherm will result in a concentration profile that exhibits a sharp leading edge and a dispersed tail, when the exponential parameter is in the range of $0 < \eta < 1$.

Next, we consider a situation involving injection of clean water into a contaminated soil system with the Freundlich exponent $\eta > 1$. For this situation the following conditions are satisfied:

$$\begin{gathered} c_o = 0 < c_i \\ \frac{df_1(c)}{dc} = \frac{\rho b_1 K_1}{\theta_1}\,\eta c^{\eta-1} > 0 \\ \frac{d^2f_1(c)}{dc^2} = \frac{\rho b_1 K_1}{\theta_1}\,\eta(\eta - 1)c^{\eta-2} > 0 \end{gathered} \tag{20}$$

which corresponds to type 2 conditions (13). These conditions lead to a concentration profile that exhibits a dispersed front and a sharp trailing edge (sharp tail). The location of the sharp tail is given by

$$z_f = \frac{\theta_1 v_1 t c_i}{\theta_1 c_i + \rho_{b_1}K_1 c_i^\eta} \qquad z_f < d_1 \tag{21}$$

The situations described above apply to a single soil layer or a homogeneous soil column. For a multilayered transport problem, continuity conditions of solute mass fluxes and concentrations at the interfaces between the adjacent layers also need to be enforced. The interfaces are fixed in space so that the volumetric fluid flux, or Darcy velocity, and solute mass flux must be continuous at $z = d_j$ at all times. When the hydrodynamic dispersion effects are ignored, the continuity requirement under steady state flow conditions may be expressed as

$$c(z_j^-, t) = c(z_j^+, t) \qquad j = 1, 2, \cdots, n - 1 \tag{22}$$

where $z_j^- = d_j - \varepsilon$, and $z_j^+ = d_j + \varepsilon$ with $\varepsilon$ being positive and infinitesimally small.

The complete solution for concentration distributions in a layered system at any time is obtained by solving the concen-

tration traveling equation (10) in each layer, subject to the continuity equation (22) in addition to the initial and source boundary conditions. However, special attention should be paid to tracking the sharp front or the sharp tail of the solute plume when they pass through the interfaces. We have developed an effective procedure to evaluate the analytical solution for concentration distributions in space and time, as discussed in the next section.

## Evaluation of the Analytical Solution

The analytical solution in this paper needs a special procedure for evaluation. Unlike a closed form analytical solution for linear solute transport in which a concentration value can be computed given a spatial variable $z$ and time $t$, the present solution describes the traveling distance for a particular concentration from the source (or a starting location) at any given time. Physically, the downstream flow and transport conditions in a layered system have no effects on the upstream solute migration. In other words, the concentration variation with time at an interface is solely determined by the transport processes in the upstream layers, and it can be described as a known time-dependent boundary condition to the adjacent downstream layer if the concentration profiles are evaluated layer by layer starting from layer 1.

The general procedure for evaluation of the solute plume using the analytical solution could be complicated if the initial concentration is nonuniform and the source boundary condition is an arbitrary function of time. Although the wave traveling equation (10) is still applicable to any layer, we have to keep tracking the new locations of both the initial concentrations of the system and the concentration values starting from the source boundary, in conjunction with determination of sharp fronts or tails of the solute plume for given isotherm functions for all layers. Fortunately for many applications such as modeling of metal transport in the subsurface, soil and aquifer systems are initially contaminant-free, and the adsorption isotherms satisfy either type 1 conditions represented by (12) or type 2 conditions represented by (13). Consequently, the evaluation of the solution is straightforward as outlined below.

1. Determine whether the isotherm curve is type 1 or type 2 by examining if $f'(c)$ (or $K_d^*$) is monotonically decreasing (type 1) or increasing (type 2) with respect to the dissolved concentration $c$ for each layer of soils with a given chemical.

2. Subdivide the source concentration $c_o$ into $nc$ intervals with $0 < c^1 < c^2 < \cdots < c^{nc-1} < c^{nc} = c_o$, and calculate theoretical arrival times of $c^k$ at interface $j$ using the following equation:

$$t_j^{c^k} = \frac{v_j(d_j - d_{j-1})}{1 + f_j'(c^k)} + t_{j-1}^{c^k} \qquad \begin{array}{l} j = 1, 2, \cdots, n-1; \\ k = 1, 2, \cdots, nc \end{array} \tag{23}$$

where $d_j$ is the distance (or depth) to the interface between layers $j - 1$ and $j$ with $d_o = 0$, and $t_0^{c^k} = 0$.

3. Determine the traveling distance of $c^k$ into the soil column for any given $t > 0$:

$$z^k = d_{j-1} + \frac{v_j(t - t_j^{c^k})}{1 + f_j'(c^k)} \qquad t_{j-1}^{c^k} < t \le t_j^{c^k}, \tag{24}$$

4. Determine whether a sharp front or a sharp tail develops during the movement of the solute plume using the following mass balance calculation: For type 1 isotherms, the sharp front $z_f$ is described as

$$\int_0^{z_f} \theta(z^k)[c(z^k, t) + f(c^k)]\, dz^k = \int_0^t V c_0(t)\, dt = m_c(t) \tag{25}$$

where

$$\theta(z^k) = \theta_j \qquad d_{j-1} < z^k \le d_j$$

and

$$m_c(t) = \int_0^t V c_0(t)\, dt$$

is the total injected mass of solute.

For type 2 isotherms, a sharp tail $z_t$ forms during freshwater flushing following a period of pulse injection $T_p$.

$$\int_{z_t}^{\infty} \theta(z^k)[c(z^k, t) + f(c^k)]\, dz^k = m_c(T_p) \tag{26}$$

Equations (25) and (26) are simply a statement of the solute mass balance within the systems. Knowing the total solute mass, the sharp front $z_f$ or the sharp tail $z_t$ can be solved numerically. The above procedure for evaluating the analytical solution has been programmed on a personal computer to provide complete concentration profiles and breakthrough curves.

## Verification and Demonstrative Examples

Three examples are provided to verify and demonstrate application of the analytical solution. The first example concerns transport in a uniform soil column. The analytical solution is compared with numerical results obtained using a one-dimensional Galerkin finite element code named HYDRUS [*Kool and van Genuchten*, 1991]. The second example involves transport in a two-layered soil system. In both examples, two cases with the Freundlich isotherm exponent $\eta = 0.5$ and 1.5 are considered in order to illustrate type 1 and type 2 conditions. The third example concerns transport of a heavy metal (lead) for which a tabular isotherm expressed in terms of $K_d^*$ versus $c$ is determined using the MINTEQA2 geochemical speciation code [*Allison et al.*, 1991].

### Example 1: Transport in a Homogeneous Soil Column

A soil column 100 cm in length is subjected to a steady infiltration of 0.2 cm/d and a pulse release of solute for a period of 10 days. The initial concentration $c_i$ and source concentration $c_o$ are 0 and 1 mg/L, respectively. The water content and bulk density of the soil material are 0.45 and 1.5 g/cm$^3$, respectively.

Two cases with the Freundlich exponent $\eta = 0.5$ and 1.5 were simulated. The Freundlich leading coefficient $K = 1$ with the units of (cm$^3$/g) (L/mg)$^{-0.5}$ and 1 (cm$^3$/g) (L/mg)$^{0.5}$, for cases 1 and 2, respectively. To obtain numerical solutions that match the pure advection assumption of the analytical solution, the molecular diffusion coefficient was set to zero, and dispersivity values required by the HYDRUS code were kept very small and equal to 0.005 cm and 0.01 cm for cases 1 and 2, respectively. Constant grid spacings and time steps were

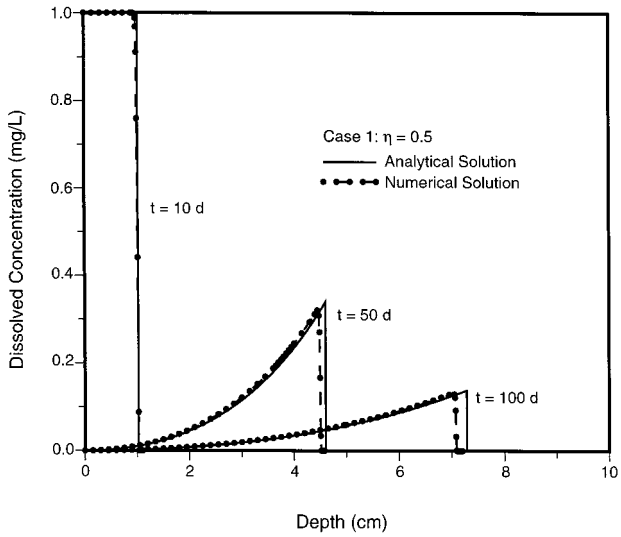


**Figure 1.** Concentration profiles for case 1 of example 1 showing comparison of analytical and numerical solutions.

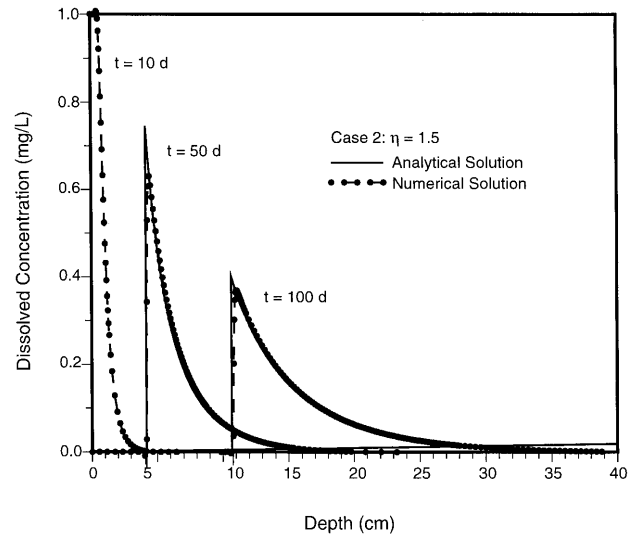


**Figure 2.** Concentration profiles for case 2 of example 1 showing comparison of analytical and numerical solutions.

used (case 1, $\Delta z = 0.01$ cm and $\Delta t = 1$ day; case 2, $\Delta z = 0.05$ cm and $\Delta t = 1$ day). The grid spacings and time steps were carefully selected to avoid numerical oscillations due to the effects of grid Peclet and Courant numbers.

Shown in Figure 1 are concentration profiles at $t = 10$, 50, and 100 days computed for case 1 ($\eta = 0.5$). As expected, when $0 < \eta < 1$, the concentration profiles exhibit sharp leading fronts and dispersed tails. This behavior is captured very well by both the analytical and numerical solutions. The two solutions are generally in excellent agreement. Note that the positions of numerical fronts at time values of 50 and 100 days lag slightly behind the analytical fronts. Furthermore, the numerical values of concentration are slightly higher than the analytical values, particularly, just behind the sharp fronts. The discrepancy between the analytical and numerical solutions may be attributed to the combined effect of physical (hydrodynamic) dispersion and artificial (numerical) dispersion on the results obtained from the HYDRUS code. The corresponding simulation results for case 2 ($\eta = 1.5$) are illustrated in Figure 2. In this situation, where $\eta > 1$, the concentration profiles exhibit dispersed fronts followed by sharp tails. The analytical and numerical solutions are also in excellent agreement.

For both situations of nonlinear adsorption the effects of hydrodynamic dispersion on simulated concentration profiles are further investigated by running the numerical model with higher-dispersivity values. The results which correspond to $\eta = 0.5$ and $\eta = 1.5$ are shown in Figures 3 and 4, respectively. Note that we select two typical time values that are much greater than the pulse duration of solute injection so that the plumes are well inside the column. Through a substantial increase of dispersivity value, we introduce more dominant influences of hydrodynamic dispersion on concentration distributions. This generally leads to smearing of the sharp front (or sharp tail) and a significant reduction of peak concentration. For the case of $\eta = 0.5$ (Figure 3) the peak location is pushed upstream with increasing dispersivity value. Consequently, the time of arrival of the peak concentration at a specific location is delayed. This behavior is consistent with the fact that when the Freundlich exponent $\eta < 1$, the adsorption and hence retardation characteristics become more pronounced at lower concentrations. Note that the reverse is true for the case of $\eta = 1.5$ as can be seen in Figure 4, which depicts the downstream shift in concentration peak with increasing dispersivity value.

**Example 2: Transport in a Two-Layer Soil Column**

This example concerns one-dimensional transport of solute through a two-layered soil column: the first layer being 100 cm thick, and the second being semi-infinite. The initial concentration is zero, and a pulse solute injection is applied for 50 days with a constant concentration of 10 mg/L, followed by continuous water injection. The Darcy velocity of fluid is constant and equal to 0.4 cm/d. The water content and bulk density are 0.4 and 1.5 g/cm$^3$ for layer 1 and 0.25 and 1.6 g/cm$^3$ for layer 2, respectively.

Two cases corresponding to type 1 and type 2 conditions were simulated. The Freundlich parameter values for both cases are as follows:

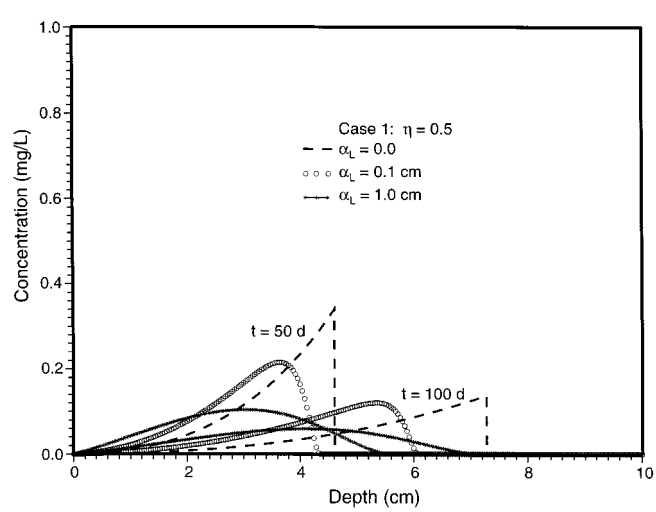


**Figure 3.** Concentration profiles for case 1 of example 1 showing the effect of hydrodynamic dispersion.

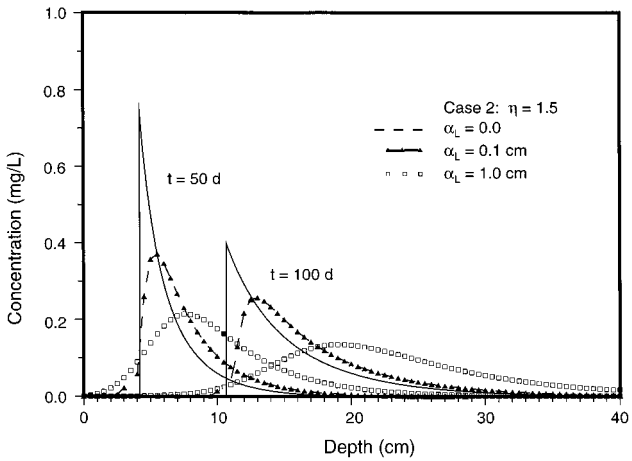


**Figure 4.** Concentration profiles for case 2 of example 1 showing the effect of hydrodynamic dispersion.

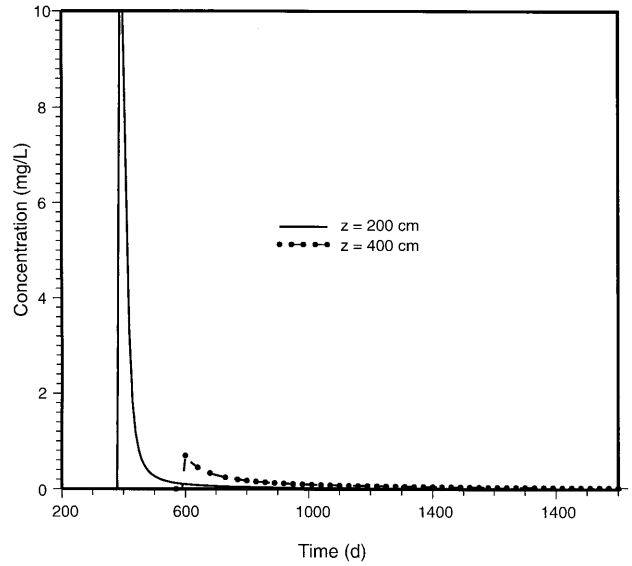


**Figure 6.** Breakthrough curves for case 1 of example 2.

Case 1
$\eta_1 = 0.45, K_1 = 0.64\ (\mathrm{cm}^3/\mathrm{g})\ (\mathrm{L/mg})^{-0.05}$
$\eta_2 = 0.05, K_2 = 0.80\ (\mathrm{cm}^3/\mathrm{g})\ (\mathrm{L/mg})^{-0.95}$

Case 2
$\eta_1 = 1.5, K_1 = 0.64\ (\mathrm{cm}^3/\mathrm{g})\ (\mathrm{L/mg})^{0.5}$
$\eta_2 = 5, K_2 = 0.25\ (\mathrm{cm}^3/\mathrm{g})\ (\mathrm{L/mg})^{4}$

Shown in Figure 5 are concentration profiles computed for case 1 using the analytical solution. Once again, the occurrence of sharp fronts followed by dispersed tails may be noted. At the interface of the soil layers ($z = 100$ cm) there is an abrupt change in the slope of the tail of concentration profile. This is because the wave traveling velocity changes across the interface because of different soil properties. The breakthrough curves at two locations in layer 2 are depicted in Figure 6. As can be seen, the discontinuity in concentration value occurs at the first arrival time value when the sharp front reaches a particular location. Thereafter the concentration declines exponentially.

For case 2, simulated concentration profiles at three typical time values are shown in Figure 7. These profiles exhibit advancing but dispersed fronts followed by sharp tails where discontinuities in concentration values occur. At the interface of the soil layers ($z = 100$ cm) the gradients of the concentration fronts change rather abruptly because of contrasting soil properties. The breakthrough curves at three locations in layer 2 are depicted in Figure 8. Each curve exhibits a smooth

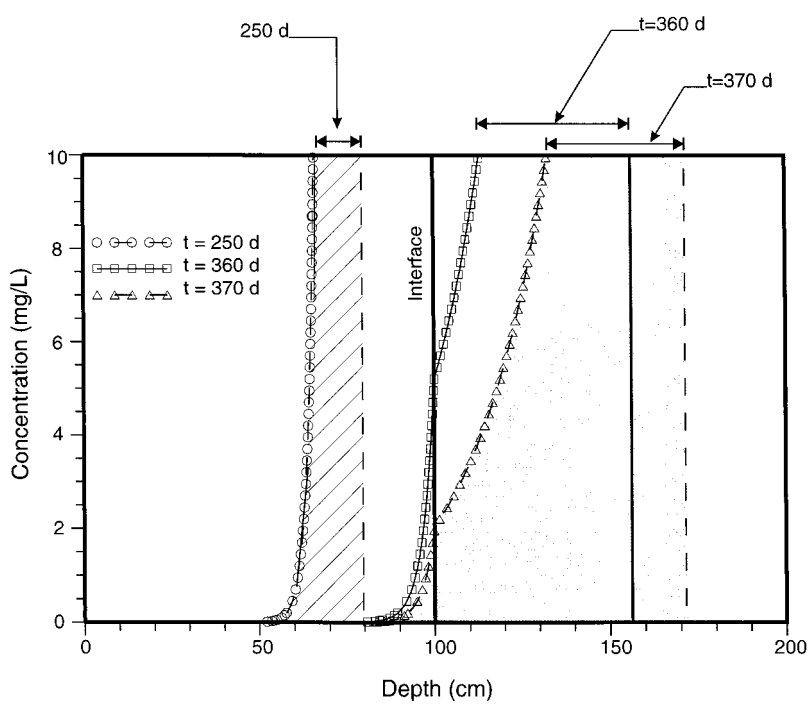


**Figure 5.** Concentration profiles for case 1 of example 2.

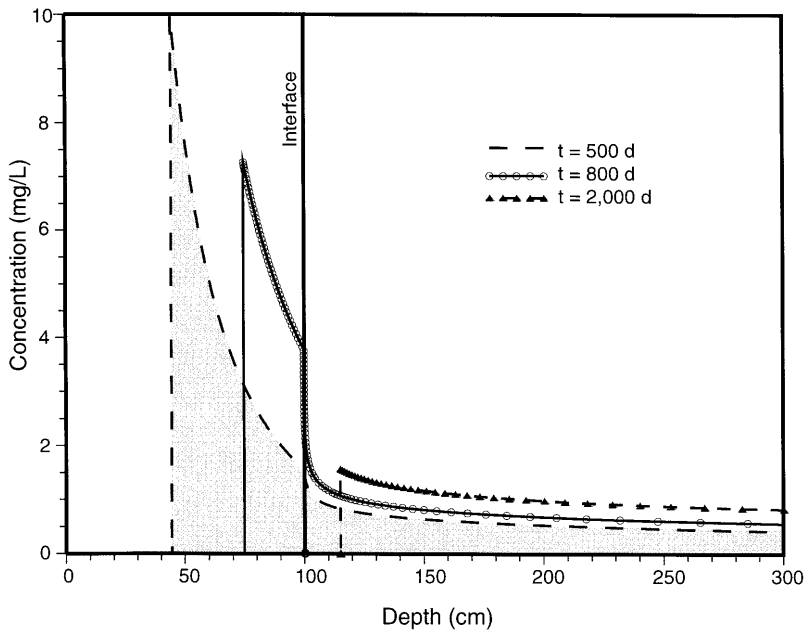


**Figure 7.** Concentration profiles for case 2 of example 2.

rise of concentration until the arrival of the sharp tail (trailing edge). At this time the breakthrough curve undergoes a sudden drop in concentration value as shown in Figure 8.

**Example 3: Metal Transport Through Unsaturated Zone**

In this example we demonstrate the utility of our analytical solution in the assessment of migration of dissolved heavy metals through the unsaturated zone of an unconfined groundwater system. It is well recognized that at high concentrations, sorption characteristics of such metals (e.g., Pb and Cr) may be highly nonlinear and strongly dependent on geochemical properties of the groundwater and soil system. Furthermore, the effective partition coefficient $K_d^*$ may decrease with increasing concentration (type 1) or increase as concentration increases (type 2), depending on the type of metal. For example, lead exhibits the first type of behavior, whereas mercury exhibits the second type.

The MINTEQA2 geochemical code [*Allison et al.*, 1991] provides in a tabular form an estimation of adsorption isotherm for a particular metal with specific geochemical conditions as indicated by parameters such as $p$H, FeO$x$, natural organic matter content, and leachate organic content. We consider a situation involving lead transport in an unsaturated zone 10 m thick. The soil system is assumed to be homogeneous, initially contaminant free, and subjected to steady infiltration at a rate of 0.45 m/yr. The average water content of the soil is 0.45, and its bulk density is 1.45 g/cm$^3$. The lead concentration at the surface source is 1 mg/L, and it is assumed that the source is removed after 10 years.

The isotherm for lead was produced by running the MINTEQA2 code. Figure 9 depicts the relationship of the

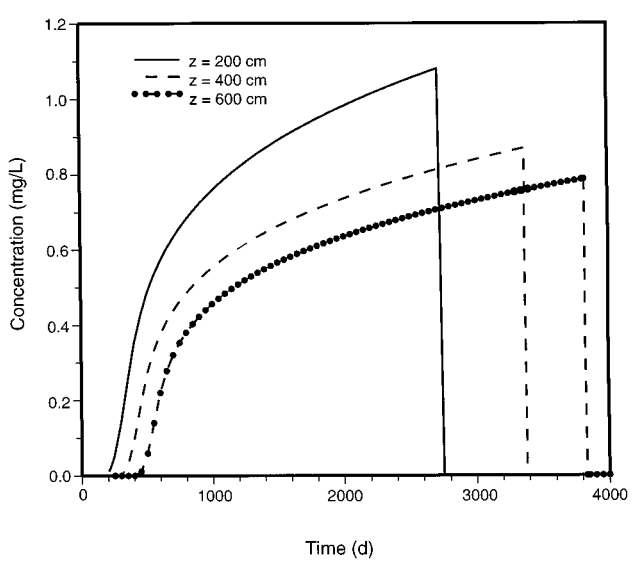


**Figure 8.** Breakthrough curves for case 2 of example 2.

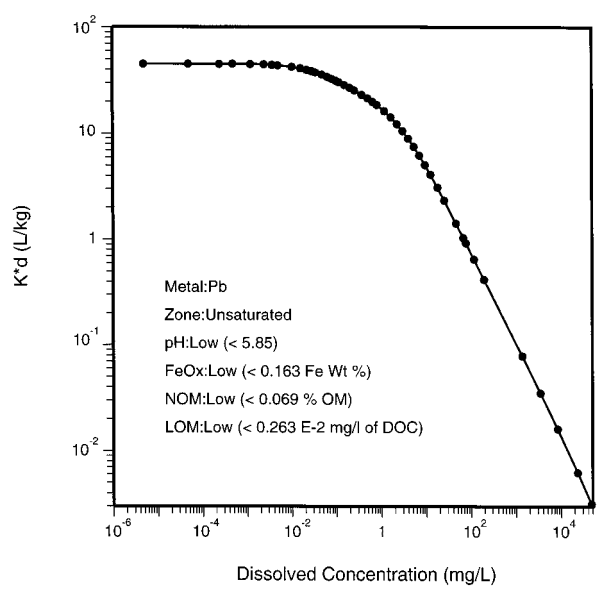


**Figure 9.** Nonlinear isotherm of lead obtained from the MINTEQA2 code.

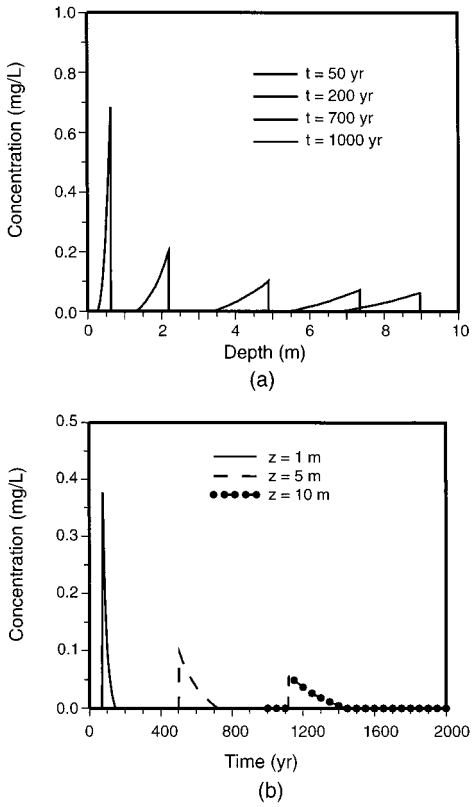


**Figure 10.** Simulation results for example 3, (a) concentration profiles, and (b) breakthrough curves.

effective partition coefficient $K_d^*$ versus concentration $c$ for low $p$H, FeO$x$, and organic content. Note that at low concentrations, $K_d^*$ is approximately constant and at the maximum value. As the concentration increases, $K_d^*$ decreases gradually at first and logarithmically thereafter. The isotherm shown in Figure 9 is somewhat similar to the Freundlich isotherm with $\eta < 1$. In the present case, however, $K_d^*$ remains at a finite value at very low concentrations.

Figure 10 shows simulated concentration profiles and breakthrough curves obtained using the analytical solution. Note that the simulation results indicate type 1 transport conditions leading to concentration profiles that exhibit sharp fronts and dispersed tails, the length of the tail being greater and the peak concentration value being smaller as time progresses. The concentration breakthrough curves exhibit first arrival time values that reflect a gradual increase of the effective partition coefficient $K_d^*$ as concentration decreases. The time of first arrival at the water table is slightly over 1100 years. As the contaminant reaches the water table, its dissolved concentration becomes so low ($c < 0.05$ mg/L) that $K_d^*$ becomes relatively constant and transport in the saturated zone may be well simulated using a linear isotherm.

## Discussion and Conclusion

An approximate analytical solution has been developed for simulating one-dimensional transport of solute with nonlinear adsorption in a multilayered soil system. The solution has been verified using a numerical code, and excellent agreement has been obtained between analytical and numerical results when dispersive effects are negligible. Some interesting phenomena have been revealed by the analytical solution. Depending on the nonlinear characteristics of adsorption isotherms, solute concentration profiles may exhibit long dispersed fronts or tails, although hydrodynamic dispersion is negligible. For pure advection cases the concentration profiles resulting from using the Freundlich isotherm exhibit sharp fronts followed by dispersed tails when the Freundlich exponent is less than unity. In contrast, when the Freundlich exponent is greater than unity, the concentration profiles are characterized by dispersed fronts and sharp tails. Through a comparative study of analytical and numerical solutions for pulse injection scenarios, the influences of hydrodynamic dispersion on concentration distributions have also been observed. In general, dispersion reduces the peak concentration and delays or speeds up the peak arrival time at a specific location, depending on whether the Freundlich exponent is less than or greater than unity. The analytical solution developed in this study describes the traveling distance for a particular concentration wave from the source at any given time. In a layered soil system an abrupt variation in soil material properties across each interface causes the wave traveling velocity to undergo an abrupt change. Consequently, concentration gradient will change abruptly across the interfaces.

The given analytical solution procedure is useable for any form of nonlinear isotherms given as closed-form functions, or tabulated data, with a general time-dependent source boundary conditions. An application has been made to unsaturated zone transport of a heavy metal. For such a case the isotherm is characterized by an effective partition coefficient which is at a maximum at low concentration values and decreases, at first gradually and then logarithmically, with increasing concentration. Owing to this behavior of isotherm, the contaminant emanating from a surface source is increasingly retarded as it moves through the unsaturated zone. The highly retarded contaminant may take a very long time (centuries) to reach the water table. Upon entering the aquifer system, the dissolved concentration becomes so low that transport in the saturated zone may be well simulated using a linear isotherm.

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