SOLUTE TRANSPORT UNDER NON-LINEAR SORPTION AND DECAY

SERGIO E. SERRANO*
Department of Civil Engineering, University of Kentucky, Lexington, KY 40506, USA

(First received 1 December 1999; accepted in revised form 1 August 2000)

Abstract—Contaminant transport in aquifers is usually represented by a solution to the advective-dispersive differential equation. When the contaminant is subject to non-linear degradation or decay, or it is characterized by a chemical constituent that follows a non-linear sorption isotherm, the resulting differential equation is non-linear. Using the method of decomposition, series solutions were obtained for the non-linear equation. The series were used to derive and test “simulant” solutions that arise using the concept of double decomposition. Simulant solutions are closed-form analytic expressions that approximate part of the series. These expressions are simple, stable, and flexible. They permit an accurate forecasting of contaminant propagation under non-linearity in laboratory or field investigations at early or prolonged times after the spill. In this article, the practical scenario of an instantaneous spill, and that of a constant concentration boundary condition, is studied for situations of non-linear decay, non-linear Freundlich isotherm, and non-linear Langmuir isotherm. The solutions are verified with limited well-known analytical solutions of the linear reactive and non-reactive equations with excellent agreement, and with limited finite difference solutions. Plumes undergoing non-linear decay experience a profile re-scaling with respect to that of linear decay, the degree of which is controlled by the magnitude of the non-linear parameter $b$. The direction of the scaling (scaling up or scaling down with respect to the linear decay plume) is controlled by the magnitude of $C$ (whether greater or less than 1) in relation to the magnitude of $b$ (whether greater or less than 1). When $C > 1$, values of $b < 1$ produce plumes that experience less decay (i.e., are scaled up) than that of the linear decay, whereas values of $b > 1$ produce non-linear plumes that experience more decay (i.e., are scaled down) than that of the linear decay. The opposite effect is observed when concentrations are less than 1. In other words, when $C < 1$, values of $b < 1$ produce non-linear plumes that experience more decay (i.e., are scaled down) than that of the linear decay, whereas values of $b > 1$, produce non-linear plumes that experience less decay (i.e., are scaled up) than that of the linear decay.

A plume undergoing non-linear sorption according to a Freundlich isotherm retards the processes of advection and dispersion with respect to a plume with no sorption. Similar to the case of non-linear decay, whether this retardation is more or less pronounced than that of the linear sorption plume depends on whether the values of $b$ and $C$ are greater or less than 1. The solution presented here for the advective dispersive equation subject to a Freundlich sorption isotherm is restricted to concentration greater than 1. When $C > 1$ and $b < 1$, the decrease in mobility in the non-linear plume is not as pronounced as that of a plume modeled by a linear isotherm. Plume shape may be quite sensitive to the values of the non-linear parameters. Plumes with parameter values $b < 1$ and $C > 1$ exhibit the well-known lack of symmetry with respect to their center of mass, sharp fronts, and the tailing effects observed at hazardous waste sites. As the magnitude of the non-linear parameter increases, the non-linear plume approaches the linear one. This partial non-linear “retardation” can now be observed quantitatively with the models presented herein. The models developed also simulate the case of $b > 1$ (i.e., “unfavorable” sorption), which produce a plume even more retarded than the linear. The shape of a contaminant plume following a non-linear Langmuir isotherm is very sensitive to the magnitude of the non-linear parameter $a$. Approximate solutions for mild non-linearity are presented. © 2001 Elsevier Science Ltd. All rights reserved

Key words—non-linear, decay, equilibrium sorption isotherm, groundwater contaminant transport, mathematical modeling

INTRODUCTION

A common approach to the simulation of transport of reactive contaminants in porous media is to assume that it is governed by a linear sorption isotherm (Fetter, 1993). However, studies have revealed that the fate and transport of many contaminants in porous media are sensitive to sorption isotherm non-linearities. Although it is not yet known the complete spectrum of chemical constituents governed by non-linearity in the sorption process when traveling through various soils, it
is suspected that the non-linear sorption may have an
effect on the shape of the plume. Non-linear sorption
may be the reason why some contaminant particles
arrive at a monitoring point faster, and some slower,
than predicted by linear models.

There is a wealth of literature regarding transport
through porous media subject to non-linear equi-
librium sorption. An excellent summary from the
point of view of chemical engineering appears in
Perry and Green (1997, Chapter 16). In the area of
environmental engineering, several studies have been
conducted (Van Genuchten and Cleary, 1982; Bolt,
1982). Weber et al. (1991) present a review of
sorption phenomena, including the effects of non-
linearity on plume shape. They concluded that the
center of mass velocity of a contaminant plume that
follows a Freundlich isotherm is significantly lower
than that of a linear plume when \( b > 1 \). The
Freundlich plume also exhibits tails that differ from
that of the linear sorption plume. Non-linear sorp-
tion is shown to have a strong effect on plume shape.

While research efforts focus on the determination of
the functional form of non-linear isotherms and
their parameter values and characteristics, the
hydrologist and the environmental engineer are also
interested in the forecasting of a plume propagation
under non-linear adsorption, given a contamination
scenario. From the monitoring, aquifer management,
and remediation design points of view, quantitative
knowledge of contaminant concentration distribution
is desirable. In addition, a mathematical model
of plume propagation should be useful in the
laboratory estimation of parameters. The prediction
of contaminant distribution in time and space may be
accomplished by solutions of the mass conservation
equation subject to a given set of initial, source, and
boundary conditions. When the dispersion equation
is subject to non-linear adsorption or decay, the
governing non-linear differential equation has tradi-
tionally been solved numerically. Analytical solutions
of the non-linear differential equation are difficult.
The most important approximate analytical solutions
focus on an asymptotic front speed and shape of
traveling waves by deriving a traveling wave equation
with a moving coordinate system. Van der Zee
(1990), Bosma and Van der Zee (1993) and Simon
et al. (1997) are representative works with this
approach. They concluded that as the magnitude of
the non-linear parameter \( b < 1 \) decreases there is an
increase in front sharpening.

In this article, we derive a decomposition series
solution (Adomian, 1994) of the non-linear advect-
dispersive-reaction equation. Decomposition
generates an analytic series, much like Fourier series,
which converges fast to the exact solution. The most
important feature of the method, however, is that if
offers the simplest systematic procedure to solve non-
linear equations without linearization or discretiza-
tion. The series solutions are verified with limited
well-known exact solutions for the linear case.

Comparisons with limited finite difference solutions
of the non-linear equation are also done. We then
explore analytic approximations to the series, called
analytic “simulant” solutions for the cases of non-
linear decay, nonlinear Freundlich isotherms, and
non-linear Langmuir isotherms. Two situations
commonly used in hydrologic laboratory and field
applications are studied: the instantaneous spill, and
the constant concentration boundary condition. The
resulting expressions are simple formulae that allow
the hydrologist the forecasting of contaminant plumes
given the laboratory-measured values of the
non-linear parameters.

DECOMPOSITION OF THE DISPERSION EQUATION
UNDER LINEAR DECAY

To illustrate the methodology, consider initially
the one-dimensional advective-dispersive equation in
an infinite aquifer subject an instantaneous point
source and linear biological or radioactive decay:

\[
\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} + aC = 0, \quad -\infty < x < \infty, \quad 0 < t
\]

\[
C(z, \infty, t) = 0, \quad C(x, 0) = C_0 \delta(x) \quad (1)
\]

where \( C(x, t) \) represents the contaminant concentra-
tion \( (M/L^3) \), \( D \) is the aquifer dispersion coefficient
\( (L^2/T) \), \( u \) is the aquifer pore velocity \( (L/T) \), \( x \) is
distance from the source \( (L) \), \( t \) time after the spill \( (T) \),
\( a \) is the capacity parameter \( (T^{-1}) \), \( C_0 \) is the initial
concentration \( (M/L) \); and \( \delta \) is the Dirac’s delta
function.

The method of decomposition offers several
approaches to the problem of decomposition of a
differential equation (Adomian, 1994, 1993), each with
distinct levels of difficulty and convergence. We
choose one that has worked in the past for similar,
although stochastic, equations (Serrano, 1996a). Let
us define the advective–dispersive differential oper-
ator, and the time-differential operator, respectively, as

\[
L_{x,t} = \left( \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} + u \frac{\partial}{\partial x} \right), \quad L_t = \frac{\partial}{\partial t} \quad (2)
\]

Equation (1) becomes

\[
L_{x,t} C + aC = 0 \quad (3)
\]

and the solution is

\[
C = -L_{x,t}^{-1} aC \quad (4)
\]

where the inverse advective–dispersive operator, \( L_{x,t}^{-1} \),
is given by the convolution integral

\[
L_{x,t}^{-1} aC = \int_0^t J_{t-\tau} aC d\tau \quad (5)
\]

and the operator \( J_t(\cdot) \) is the strongly continuous
semigroup associated with equation (2) and it is given by

\[
J_t f = \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} e^{-\frac{(x-x')^2}{4Dt}} f dx' \quad (6)
\]
Let us expand $C$ on the right-hand side of equation (4) as the series $C = C_0 + C_1 + C_2 + \cdots$. The first term in the series is

$$C_0 = L^{-1}_x aC_0 = \frac{C_1 e^{-(x-w)^2/4Dt}}{\sqrt{4\pi Dt}}$$

which is the fundamental solution or Green’s function of the advective-dispersive equation. The second is

$$C_1 = -L^{-1}_x aC_0 = -\frac{atCe^{-(x-w)^2/4Dt}}{\sqrt{4\pi Dt}}$$

The third is

$$C_2 = -L^{-1}_x aC_1 = \frac{\partial^2 C}{\partial x^2} \frac{Ce^{-(x-w)^2/4Dt}}{\sqrt{4\pi Dt}}$$

In general, the $n$th term is given by

$$C_n = -L^{-1}_x aC_{n-1} = (-1)^n \frac{(at)^n}{n!} \frac{Ce^{-(x-w)^2/4Dt}}{\sqrt{4\pi Dt}}$$

Thus, the solution to equation (1) is

$$C = \sum_{n=0}^{\infty} C_n = \frac{C_0 e^{-(x-w)^2/4Dt-at}}{\sqrt{4\pi Dt}}$$

which is the well-known solution to the advective-dispersive equation with linear decay. The same result is obtained if instead of equation (2) we operate equation (1) with $L$, which sometimes yields simpler integrals in the series. This is the case when complex boundary conditions are involved or when the pore velocity and dispersion coefficients are given as explicit functions of the recharge and the statistical properties of the hydraulic conductivity field (Serrano, 1996b; Serrano and Adomian, 1996). In either case, decomposition series converge to the exact solution to the differential equation. In many instances, however, the closed-form solution may not be identified. This is especially true in many non-linear equations. While a closed-form solution is mathematically desirable, the series solution constitutes an accurate model of interest to the practicing hydrologist.

CONTAMINANT TRANSPORT UNDER NON-LINEAR DECAY

In cases of non-linear biological or radioactive decay, equation (1) becomes

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} + aC^b = 0$$

where $b$ is the non-linearity parameter. As before, let us write the solution of equation (12) as

$$C = C_0 - aL^{-1}_x NC, \quad NC = C^b$$

where the non-linear operator, $N$, is expanded as

$$C = C_0 - aL^{-1}_x \sum_{n=1}^{\infty} A_n$$

and the Adomian polynomials are defined as

$$A_0 = NC_0, \quad A_1 = \frac{dNC_0}{dC_0}$$

$$A_2 = C_1 \frac{d^2 NC_0}{dC_0^2} + \frac{C_1^2 d^2 NC_0}{2! dC_0^2}$$

$$A_3 = C_1 \frac{d^3 NC_0}{dC_0^3} + \frac{C_1^2 C_2 d^3 NC_0}{3! dC_0^3} + \frac{C_1^2 d^3 NC_0}{3! dC_0^3}$$

The polynomials $A_n$ are generated for each non-linearity so that $A_0$ depends only on $C_0$, $A_1$ depends only on $C_0$ and $C_1$, $A_2$ depends only on $C_0$, $C_1$, $C_2$, . . . . All of the $C_n$ components are analytic and calculable. $\sum_{n=0}^{\infty} C_n$ constitutes a generalized Taylor series about the function $C_0$, which approach zero as $1/(mn)!$, if $m$ is the order of the highest linear differential operator. Sometimes the magnitude of the aquifer parameters are such that the series converges rapidly and the $n$-term partial sum $\Phi_n = \sum_{j=0}^{n-1} C_j$, called “the approximant”, serves as an accurate enough and practical solution. For further discussion on the convergence problem of decomposition series the reader is referred to Abbaoui and Cherruault (1994), Cherruault (1989), and Cherruault et al. (1992). It is also important to mention the rigorous mathematical framework for the convergence of decomposition series developed by Gabet (1992, 1993, 1994). He connected the method of decomposition to well-known formulations where classical theorems (e.g., fixed-point theorem, substituted series, etc.) could be used. For a discussion on the convergence of decomposition series of convection-diffusion equations see Serrano (1998).

From equations (5), (6), (14) and (15), and after solving the corresponding integrals, one obtains the series

$$C = C_0 \left\{ 1 - \frac{2atC_0^{b-1}}{(b+1)} + \frac{2a^2t^2C_0^{2b-2}}{(b+1)(b-1)} - \cdots \right\}$$

This series suggest that an approximate closed-form function is plausible. Let us operate equation (12) with $L$:

$$L C = L \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} - aNC, \quad NC = C^b$$

or

$$C = DL^{-1}_x \frac{\partial^2 C}{\partial x^2} - uL^{-1}_x \frac{\partial C}{\partial x} - aL^{-1}_x NC$$

As before, we expand $C$ as $C_0 + C_1 + C_2 + \cdots$. Using equation (15), we approximate equation (18) as

$$C \approx DL^{-1}_x \frac{\partial^2 C_0}{\partial x^2} - uL^{-1}_x \frac{\partial C_0}{\partial x} - aL^{-1}_x C_0^b$$

$C_0$, may be found by using the concept of double decomposition. We expand $C_0 = \sum_{n=0}^{\infty} C_{0n}$ in the two terms on the right-hand side of equation (19),
With $C_0 = C_0 \delta(x)$, the initial condition, it is easy to show that the series
\[
C_0 = DL_t^{-1} \frac{\partial^2}{\partial x^2} \sum_{m=0}^{\infty} C_{0m} - uL_t^{-1} \frac{\partial}{\partial x} \sum_{m=0}^{\infty} C_{0m}
\]
converge to equation (7) (i.e., the Green’s function of the advective–dispersive equation). Now, equation (19) may be written as
\[
C \approx C_0 - aL_t^{-1} NC_0
\]
Note that $L_t^{-1} = \int_{0}^{t} \phi(t) \, dt$ is simpler than $L_{x,t}^{-1}$. Using equation (15), expanding, and solving the integrals, we arrive at the closed-form expression (omitting algebra details)
\[
C(x, t) \approx C_0(x, t) e^{2atC_0(x, t)t^{b-1}/(b+1)}, \quad b > 0
\]
We remark that equation (22) is not the exact solution of equation (12) since higher-order terms present in the complete expansion (13), and its series (16), are not included. Equation (22) is the “analytic simulant” of $C$ (Adomian, 1994) since it satisfies part of the complete series. It is an excellent approximation to the non-linear solution. We first test equation (22) with respect to known exact solutions of the advective–dispersive equation. In the absence of decay, $a = 0$ and equation (22) is identical to the exact solution (7). For the case of linear decay, $b = 1$, and equation (22) is identical to the exact solution of equation (1), that is equation (11). The second set of tests consisted in a comparison of the simulant solution (22) with respect to the non-linear series solution (16). Depending on the values of the parameters, the simulation time step, $t$, needs to be adjusted to assure uniform convergence of the series. With this provision, extensive numerical tests suggested that equations (16) and (22) are virtually indistinguishable for the same situation depicted in Fig. 2, except that the initial concentration has been reduced to $C_0 = 1$ mg/L. Since the concentrations are less than 1, and $b < 1$, most of the linear plume is scaled down with respect to the linear decay plume. CHemicals with low concentrations, such as those observed in laboratory column experiments (i.e., $C \ll 1$, while keeping $b < 1$) should experience greater decay than that of linear plumes. This situation is simulated with the models presented in this article. Figure 2 shows the concentration vs. distance profile one month after the spill when no decay is present, according to equation (7); when linear decay is present, according to equation (11) or (17) setting $b = 1$; and when non-linear decay is present, according to equation (22) setting $b = 0.6$. We remark that this comparison is qualitative and cannot be used to assess the effect of the non-linear parameter $b$, since the parameter $a$ has dimensions affected by $b$. Yet, the graph shows the physical bounds of the plume. In general, non-linear decay scales down the concentration profile, the degree of which is controlled by the magnitude of $b$. Since the concentrations are greater than 1 and $b < 1$, most of the linear plume is scaled up with respect to the linear decay plume.

For instance, consider a long aquifer contaminated by an instantaneous point spill with the following characteristics: $C_i = 100$ mg/L, $D = 1$ m$^2$/month, $a = 1$ m/month, $t = 1$ month, $a = 1$ (mg/L)$^{1-b}$ month$^{-1}$, $b = 0.6$. With a decay parameter $b < 1$, the non-linear decay curve has the shape shown in Fig. 1, which illustrates the fact that for concentration less than 1, the amount of substance decayed is greater than that exhibited by a linear decay rate. Conversely, for concentrations greater than 1, the amount of substance decayed is less than that exhibited by a linear decay rate. Thus, when $b < 1$ spilled chemical with large concentrations ($C \gg 1$) should experience less decay than that of linear plumes. This situation is simulated with the models presented in this article. Figure 2 shows the concentration vs. distance profile one month after the spill when no decay is present, according to equation (7); when linear decay is present, according to equation (11) or (17) setting $b = 1$; and when non-linear decay is present, according to equation (22) setting $b = 0.6$. We remark that this comparison is qualitative and cannot be used to assess the effect of the non-linear parameter $b$, since the parameter $a$ has dimensions affected by $b$. Yet, the graph shows the physical bounds of the plume. In general, non-linear decay scales down the concentration profile, the degree of which is controlled by the magnitude of $b$. Since the concentrations are greater than 1 and $b < 1$, most of the linear plume is scaled down with respect to the linear decay plume. We see that the degree of scaling is controlled by the magnitude of $b$. The direction of the scaling (i.e., scaling up or scaling down with respect to the linear decay plume) is controlled by the magnitude of $C$ (whether greater or less than 1) in relation to the magnitude of $b$ (whether greater or less than 1). Thus, when $b > 1$, the non-linear decay curve in Fig. 1 would actually be a convex upward shape, such that for $C < 1$ there is less decay than that of the linear, and for $C > 1$ there is more decay than that of the linear curve. Correspondingly, the sense in plume scaling would be the
opposite of that shown in Figs 2 and 3. In other words, when \( b > 1 \), the non-linear plume in Fig. 2 would experience more decay (i.e., scaled down) than that of the linear plume (\( C > 1 \)); whereas the non-linear plume in Fig. 3 would experience less decay (i.e., scaled up) than that of the linear plume (\( C < 1 \)). This dependency of plume shape and scaling direction is unique and a dimensionless representation is possible.

**CONTAMINANT TRANSPORT SUBJECT TO A NON-LINEAR FREUNDLICH SORPTION ISOTHERM**

Consider the case of contaminant dispersion in a long aquifer subject to a general non-linear Freundlich isotherm of the form (Fetter, 1993)

\[
C_s = K_F C^b
\]

(23)

where \( C_s \) is the solid-phase contaminant concentration \((M/M)\), \( K_F \) is the Freundlich capacity parameter \((M/M/(M/L)^{-b})\); and \( b \) is the site energy heterogeneity factor or non-linearity factor. If \( b = 1 \), \( K_F = K_d \) the linear distribution coefficient. Equation (1) becomes

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \frac{r}{\rho_b K_F} \frac{\partial C}{\partial t} + r b C^{b-1} \frac{\partial C}{\partial t} = 0,
\]

(24)

where \( r = \rho_b K_F / n \); \( \rho_b \) is the soil dry bulk density \((M/L^3)\); and \( n \) is the porosity.

As before, we write equation (24) as

\[
C = C_0 - r b L^{-1} NC, \quad NC = C^{b-1} \frac{\partial C}{\partial t}
\]

(25)

From equations (5), (15) and (25), the second term in the decomposition series is

\[
C_1 = -r b \int_0^t J_{r,t} C_0^{b-1} \frac{\partial C_0}{\partial t} \, dt
\]

(26)

Using equations (6) and (7), expanding and solving, the Volterra integral equation (26) yields

\[
C_1 = r b C_0^b \left\{ \frac{1}{2} \frac{tx}{D} \left[ \sqrt{\frac{4t}{D}} \phi(x, t) \right]^2 \right\}
\]

(27)

Higher-order terms in the series are obtained in a similar manner. As in the previous section, we used the concept of double decomposition in conjunction with the \( t \)-partial solution to arrive at a closed-form analytic simulant of the form

\[
C \approx C_p e^{-x - \phi(t) \sqrt{4Dt} / \phi(t)}, \quad C_i \gg 1
\]

\[
\phi(x, t) = \sqrt{\frac{4Dt}{\pi}}
\]

\[
\psi(x, t) = \left\{ \frac{1}{2} \text{erfc} \left( \frac{x - ut}{\sqrt{4Dt}} \right) + \frac{e^{\frac{ux}{D}}}{2} \text{erfc} \left( \frac{x + ut}{\sqrt{4Dt}} \right) \right\}^b
\]

(28)

where \( \text{erfc}( \cdot) \) denotes the “error function complement”; and \( 2D\phi(x, t) \) is the spatially distributed, time-dependent, plume variance. We tested equation (28) in a manner similar to the decay equation in the previous section. First, with respect to known analytical solutions. For the case of no sorption, \( b = 0 \) and equation (28) is identical to the exact solution (7). For the case of linear sorption, \( b = 1 \), \( \phi(t) \) becomes \( t/R \), where \( R = 1 + rb \) the retardation
factor of linear sorption, and equation (28) is identical to the exact solution with linear decay (11) \((a = 0)\). Now, the comparison with respect to the non-linear series solution, extensive numerical experimentation indicated that equation (28) is virtually undistinguishable from the general decomposition series calculated for parameter values that assure its uniform convergence. Finally, comparison with limited finite-difference solutions of equation (24) indicated that the center of mass and the portions of the plume that exhibit high concentrations are in excellent agreement. However, the tails of the plume resulted in some discrepancy, with those predicted by equation (28) appearing as less retarded (see Fig. 5). However, a finite difference solution may not be regarded as the exact solution, since by definition it is a numerical linearization solution to the differential equation (28) may be used for the forecasting of plume evolution for early or prolonged times, and for the estimation of parameters in column or field experiments.

As an illustration, consider the chemical spill of Section 3, but instead of decay assume the contaminant is subject to sorption that fits a highly non-linear Freundlich isotherm with \(K_F = 0.001 \text{mg/g/(mg/L)}^b\), and \(b = 0.6\). Assume \(\rho_b = 1000 \text{ Kg/m}^3\), and \(n = 0.1\). Contaminant spatial distribution is desired at \(t = 360\) months (prolonged contamination), and correspondingly the scale effect of the field dispersion coefficient is large (i.e., \(D = 10 \text{ m}^2/\text{month}\)). It is assumed that the initial concentration for sorbing and non-sorbing plumes is equal to 100 mg/L, which implies that more mass is injected for the former. Clearly, we consider here the situation of a large chemical spill in the field. Figure 4 shows the concentration vs. distance profile. Again the comparison between linear \((R = 1 + rb)\) and non-linear profiles is only qualitative since the dimensions of \(K_F\) depend on \(b\). Yet it is possible to see that when \(b < 1\) and \(C > 1\) the non-linear plume suffers retardation of the processes of advection and dispersion, but not as severe as that of the linear plume. This retardation reduces the velocity of the plume center of mass and the plume variance, the degree of which is controlled by the magnitude of \(b\). The same observations related to non-linear decay in the previous section are applicable here: if one interprets Fig. 1 as a Freundlich isotherm with \(b < 1\), portions of the non-linear plume with \(C > 1\) suffer less sorption (i.e., less retardation, or more mobility) than that of the linear plume.

Figure 4 also shows that when \(b > 1\) and \(C > 1\): the time-breakthrough concentration curve showed the linear plume arriving much earlier in time than the non-linear plume, indicating that the non-linear plume was more retarded than the linear. When \(C < 1\), the effect of \(b\) on plume shape with respect to the linear plume is expected to be the opposite of that when \(C1\) as a result of the non-linear relationship between sorption and concentration. However, equation (28) is insensitive to the former and for these reasons the model is restricted to the latter case.

Figure 4 also shows the well-known phenomenon the non-linear plumes tend to be non-symmetric. Thus, equation (28) reproduces the well-known features of Freundlich sorption, namely the sharp leading edges and the "tailed" hind edges.

An important application in laboratory tests designed for parameter estimation, is the case of long-column experiments with constant source boundary condition. In this case, an analysis similar to the above leads to an analytic simulant of the form

\[
C \approx C_1 \frac{1}{2} \left( \text{erfc} \left( \frac{x - u \phi(t)}{\sqrt{4D\phi(t)}} \right) + e^{(\alpha x/D)} \text{erfc} \left( \frac{x + u \phi(t)}{\sqrt{4D\phi(t)}} \right) \right), \quad 0 \leq x < \infty, \\
C_1 \gg 1
\]

where \(C_1\) is the concentration at the boundary, and \(\phi(x, t)\) as in equation (28). Figure 5 shows the concentration spatial distribution in a semi-infinite aquifer after a time \(t = 360\) month and a comparison with a finite-difference solution of equation (24) for \(b = 0.6\). The same parameter values of Fig. 4 were used. In this situation \((b < 1\) and \(C > 1\), the contaminant front of the non-linear plume is substantially delayed, but not as much as that of
the linear sorption plume. Notice again the non-symmetry of the non-linear plume that produces a front sharper than that of the no sorption plume, but not as much as that of the linear plume. Several previous studies have concluded that as the value of \(b\) decreases (\(b<1\)) the non-linear front becomes sharper (i.e., \(\text{van der Zee, 1990}\)) (see Fig. 5).

**CONTAMINANT TRANSPORT SUBJECT TO NON-LINEAR LANGMUIR SORPTION ISOTHERM**

Consider now the case of contaminant dispersion in a long aquifer subject to a non-linear Langmuir isotherm of the form (Fetter, 1993)

\[
C_s = \frac{\alpha \beta C}{1 + \alpha C} \quad (30)
\]

where \(\alpha\) is an absorption constant related to binding energy \(E^L/M\); and \(\beta\) is the maximum amount of solute that can be absorbed by the solid \((M/M)\). The transport equation becomes

\[
\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u(x) \frac{\partial C}{\partial x} + \frac{r_1}{(1 + 2C)^2} \frac{\partial C}{\partial t} = 0, \quad (31)
\]

Equation (31) was subjected to the same analysis as described in the previous sections. We omit the lengthy algebraic manipulation necessary for the derivation of the decomposition series, the double decomposition series, and ultimately the analytic derivation of the decomposition series, the double.

Consider now the case of contaminant dispersion in an aquifer. Consider an instantaneous spill of a Langmuir-sorptive contaminant in a long aquifer with the following characteristics: \(x = 0.001\) L/mg, \(\beta = 1\) g/Kg, \(\rho_x = 1\) 000 Kg/m^3, \(D = 1\) m^2/month, \(u = 1\) m/month, \(C_i = 10,000\) mg/L, \(n = 0.1\), and \(t = 10\) month. The initial condition is exaggerated here to emphasize the differences between linear and non-linear effects, since our approximation (32) is limited to mild non-linearities.

Figure 6 shows the concentration spatial distribution in the absence of sorption according to equation (7); the concentration profile modeled by the solution to the transport equation subject to linear sorption (i.e., equation (28) with \(\phi = t/(1 + r_1)\)); and the concentration profile subject to Langmuir sorption according to equation (28) with \(\phi\) given by equation (32). As explained before, each Langmuir parameter has dimensions independent of the magnitude of the other parameter. Thus, this figure indeed shows the quantitative effect of non-linearity on the shape of the plume. As expected, non-linearity causes a
decrease in the velocity of the plume center of mass, and a corresponding increase in the magnitude of the maximum concentration with respect to the no sorption plume. This reduction in the center of mass, and corresponding increase in maximum concentration, is not as drastic as that of the linear plume. As \( a \) increases in value, there is more sorption at low concentrations. This phenomenon can be inferred intuitively from the observation of a Langmuir isotherm plotted simultaneously with a linear one. The most “retarded”, or the least mobile, is the linear one, and the most mobile, or the most dispersive, is the one without sorption. However, with the models introduced in this article, the hydrologist now has simple tools to evaluate quantitatively the effect of non-linearity.

Figure 7 further illustrates this concept. It shows the profiles of the same plume, each with a different value of the non-linear parameter \( a \) for \( t = 24 \) months. The shape of the plume may be quite sensitive to the size of non-linearity. Again, as \( a \) increases in magnitude, there is more sorption at low concentrations (see Fig. 8). Figure 8 shows the same situation depicted in Fig. 7, except that now the contaminant propagates in a semi-infinite aquifer subject to a constant source boundary condition, \( C_i \). The profiles were calculated for \( t = 10 \) month with equation (29) using equation (32) for the evaluation of \( f \).

**SUMMARY AND CONCLUSIONS**

Using the method of decomposition, series solutions were constructed for the advective-dispersive transport equation in aquifers subject to either non-linear decay, non-linear Freundlich sorption, or non-linear Langmuir sorption. Using the concept of double decomposition, the series were used to obtain analytical simulant solutions, which are closed-form expressions of part of the parent series. The analytic simulants were tested for numerical accuracy with respect to the parent non-linear series solution with an excellent agreement. They were also tested with limited known solutions to the linear equations (i.e., the simulants become the exact linear solutions when the parameters make the decay, or the isotherm, linear). The new simulant solutions are simple expressions that can be used for the forecasting of contaminant dispersion under non-linear reactions, or for the quantitative description of the effect of non-linearity in the sorption parameters, on the time-space distribution of the contaminant. The proposed models are flexible, stable, and could be used for laboratory or field simulations at early, or prolonged contamination scenarios. Two cases of practical interest in hydrology were considered: the case of an instantaneous point chemical spill in an infinite aquifer, and the case of a constant source boundary condition in a semi-infinite aquifer.
Plumes undergoing non-linear decay experience a profile re-scaling with respect to that of linear decay, the degree of which is controlled by the magnitude of the non-linear parameter $b$. The direction of the scaling (scaling up or scaling down with respect to the linear decay plume) is controlled by the magnitude of $C$ (whether greater or less than 1) in relation to the magnitude of $b$ (whether greater or less than 1). When $C > 1$, values of $b < 1$ produce plumes that experience less decay (i.e., are scaled up) than that of the linear decay, whereas values of $b > 1$ produce non-linear plumes that experience more decay (i.e., are scaled down) than that of the linear decay. The opposite effect is observed when concentrations are less than 1. In other words, when $C < 1$, values of $b < 1$ produce non-linear plumes that experience more decay (i.e., are scaled down) than that of the linear decay, whereas values of $b > 1$, produce non-linear plumes that experience less decay (i.e., are scaled up) than that of the linear decay.

A plume undergoing non-linear sorption according to a Freundlich isotherm retards the processes of advection and dispersion with respect to a plume with no sorption. Similar to the case of non-linear decay, whether this retardation is more or less pronounced than that of the linear sorption plume depends on whether the values of $b$ and $C$ are greater or less than 1. The solution presented here for the advective dispersive equation subject to a Freundlich sorption isotherm is restricted to concentration greater than 1. When $C > 1$ and $b < 1$, the decrease in mobility in the non-linear plume is not as pronounced as that of a plume modeled by a linear isotherm. Plume shape may be quite sensitive to the values of the non-linear parameters. Plumes with parameter values $b < 1$ (and $C > 1$) exhibit the well-known lack of symmetry with respect to their center of mass, sharp fronts, and the tailing effects observed at hazardous waste sites. As the magnitude of the non-linear parameter increases, the non-linear plume approaches the linear one. This partial non-linear “retardation” can now be observed quantitatively with the models presented herein. The models developed also simulate the case of $b > 1$ (i.e., “unfavorable” sorption), which produce a plume even more retarded than the linear.

The shape of a contaminant plume following a non-linear Langmuir isotherm is very sensitive to the magnitude of the non-linear parameter $z$. For values of $z$ tending to zero the plume modeled according to a Langmuir isotherm tends to coincide with that with no sorption. As the magnitude of $z$ increases, the shape of the plume is affected by showing more sorption at lower concentrations. However, the approximate analytical models presented here are not capable of predicting the form of a contaminant plume when the initial concentration is large and at the same time $z$ is large, or when $z > C$. More research is needed on the identification of simple solutions for the latter conditions.

Acknowledgements—The support and encouragement of the National Science Foundation, Grant No. BES 9710587, is greatly appreciated.

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