MASTERS PLAN B REPORT

USER GUIDE FOR EXCEL/MATLAB PROGRAM FOR
ANALYTICAL MODELS FOR CUMULATIVE MASS COLUMN TESTING

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$A =$ total (solids plus voids) cross sectional area perpendicular to the direction of flow

$BTC =$ break through curve

$C =$ Carslaw and Jaeger constant

$c_e =$ effluent concentrations of chemical species

$CMR =$ Cumulative Mass Ratio

$c_o =$ known concentrations of chemical species

$c_r =$ the resident concentration or solute concentration in the pore water of the soil

$c_r(L,t) =$ resident solute concentration at the end of the column

$D_o =$ the aqueous-phase or free-solution diffusion coefficient for the solute

$D^* =$ the effective diffusion coefficient (= $\tau_o D_o$) for solute diffusion in porous media

$D_h =$ the hydrodynamic dispersion coefficient

$D_m =$ the mechanical dispersion coefficient

$erfc =$ the complementary error function

$h =$ total hydraulic head

$i =$ the dimensionless hydraulic gradient

$i_c =$ the concentration gradient

$J =$ total solute mass flux

$J_a =$ advective mass flux

$J_d =$ diffusive solute mass flux

$J_m =$ mechanical dispersive flux

$J_{ss} =$ the solute mass flux at steady-state for the case of a constant-source concentration

$K =$ hydraulic conductivity

$L =$ the straight-line, macroscopic distance between two points defining the flow path
\( L_e \) = the actual, microscopic distance of transport between the same two points

\( n \) = total porosity

\( n_e \) = effective porosity

\( P_L \) = Péclet number

\( Q \) = volumetric flow rate

\( RC \) = relative concentration

\( R_d \) = retardation factor

\( RF \) = relative solute mass flux

\( t \) = time

\( T \) = Pore volume of flow

\( (T-CMR)_{ss} \) = the extension of the trend in \( T \) versus \( T-CMR \) at steady-state transport to the \( T-CMR \) axis

\( T_o \) = the extension of the trend in \( T \) versus \( CMR \) at steady-state transport to the \( T \)-axis

\( T_i \) = initial pore volume of flow

\( T_{inc} \) = incremental pore volume of flow

\( T_{max} \) = maximum pore volume of flow

\( T_r \) = dimensionless reactive time

\( T_{ss} \) = the pore volumes of flow required to achieve steady-state transport

\( v \) = Darcy velocity (a.k.a liquid flux)

\( v_s \) = seepage velocity

\( x \) = direction of flow

\( \alpha_L \) = the longitudinal dispersivity

\( \alpha_m \) = eigenvalue, alpha root required for Model 3

\( \beta \) = empirically determined constant between 1 and 2
\[ \beta_m = \text{eigenvalue, beta root required for Model 4} \]

\[ \frac{\partial c_r}{\partial x} = \text{concentration gradient based on the resident concentration} \]

\[ \tau_a = \text{the apparent tortuosity factor} \]

\[ \tau_g = \text{the geometric (or matrix) tortuosity factor} \]
CHAPTER 1 INTRODUCTION

An understanding of the transport of aqueous miscible contaminants in porous media is important in many applications related to geoenvironmental engineering, including applications pertaining to the design and construction of waste containment facilities and applications related to remediation of pre-existing contaminated sites. Historically, laboratory column testing has been used to measure relevant contaminant transport parameters for such applications. Unfortunately, the parameters measured from small-scale laboratory columns generally are not considered representative of the field due to the inherent heterogeneity of the soil at field scales and the discrepancy between the field and laboratory scales (e.g., Gelhar et al. 1992). However, these issues do not exist, or exist to a far lesser extent, in the case of engineered barrier systems, such as compacted clay liners and soil-bentonite (SB) vertical cutoff walls, because the material compositions are controlled and the typical thicknesses of barriers (≤ 1 m) can be reproduced in the lab. As a result, column testing has been used to aid in the design and evaluation of contaminant barriers (Crooks and Quigley, 1984; Yong et al. 1986; Acar and Haider, 1990; van Ree et al. 1992).

Traditional column testing procedures typically involve (1) establishing steady state flow through a column comprised of the porous media to be tested, (2) continuously injecting a chemical solution of a known solute concentration \( c_o \) into the influent, and (3) measuring the concentration \( c_e \) of the same solute in the effluent as a function of time. The literature is replete with examples of this procedure (e.g., Freeze and Cherry, 1979; Shackelford, 1991; Shackelford, 1993; Shackelford 1995 a,b; Schwartz and Zhang, 2003). More recently, an alternative approach to column testing involving consideration of the cumulative solute mass emanating from the
column instead of the effluent concentration has been proposed (Shackelford 1995a,b). In this regard, Shackelford (1995b) compared and contrasted four analytical models typically used in analyzing column test data from the traditional approach in the forms required for analyzing the data resulting from the cumulative mass approach.

Accordingly, the purpose of this study was to program both the concentration-based and the cumulative-mass based analytical models presented and compared by Shackelford (1995b) in the form of Excel and Matlab programs, as these commercially available software programs are commonly used nowadays. The four programs were developed based on four analytical models that describe the concentration of aqueous miscible solutes as a function of space and time [i.e., \( C(x,t) \)] during one-dimensional solute transport through porous media under steady-state solvent flow conditions. The analytical models differ in terms of the different boundary conditions upon which they were originally derived. Also, each analytical model for \( C(x,t) \) can be manipulated mathematically to generate associated analytical models describing the spatial and temporal variation in solute mass flux, \( J(x,t) \), and the temporal variation of cumulative mass of solute that has migrated through the effluent end of a porous medium of length, \( L \), or \( \Sigma m(L,t) \). Thus, for each set of boundary conditions, there are a total of three models describing \( C(x,t) \), \( J(x,t) \), and \( \Sigma m(L,t) \), resulting in a total of 12 analytical models. Shackelford (1995b) previously derived and published the models for \( J(x,t) \) and \( \Sigma m(L,t) \) for the purpose of evaluating the differences in the models in terms of their use in determining the dispersion/diffusion coefficient, \( D \), and the retardation factor, \( R_d \), based on the results of column tests using the cumulative mass approach. However, Shackelford (1995b) programmed all 12 models using the FORTRAN (FORmula TRANslation) computer language which is still used but is no longer commonly taught in engineering curriculums. As a result, the 12 models were programmed into the Excel (Version
14.0.4763.1000, 2010, Microsoft Corporation, Redmond, WA) and Matlab (Version 7.11.0.584, R2010b, MathWorks, Natick, MA) commercially available softwares which will be a more user friendly with current engineering curriculums. The developed Excel and Matlab programs were validated against the results published by Shackelford (1995b). A user guide has been developed for the Excel and Matlab programs to assist the user with operating the program.

Simulations using the developed programs with a range of transport parameters were performed to compare the effects of retardation and the diffusion/dispersion coefficient on the four analytical models. These comparisons are presented to illustrate the use of the programs.
CHAPTER 2 THEORETICAL BACKGROUND

2.1 Solute Mass Flux

*Advection* is the process whereby solutes are transported along with the flowing liquid (solvent) due to a hydraulic gradient. The rate at which a solute is transported is equal to the average linear velocity of the liquid (solvent), also commonly termed the seepage velocity, $v_s$. The seepage velocity corresponds to the liquid flow that occurs only within the connecting void spaces of a porous medium and, therefore, is given by the quotient of the *Darcy velocity*, $v$, and the effective porosity, $n_e$, or:

$$ v_s = \frac{v}{n_e} \tag{2.1} $$

where $v$ is defined by Darcy's law as follows:

$$ v = \frac{Q}{A} = -K \frac{\partial h}{\partial x} = Ki \tag{2.2} $$

where $Q = \text{volumetric flow rate}$ of the liquid, $A = \text{total (solids plus voids) cross sectional area perpendicular to the direction of flow}$, $K = \text{hydraulic conductivity}$, $h = \text{total hydraulic head}$, $x = \text{direction of flow}$, and $i = \text{the dimensionless hydraulic gradient}$. The Darcy velocity also is commonly referred to as the *liquid flux*. The effective porosity, $n_e$, defined as the volume of the pore space that actually conducts liquid flow divided by the total volume (void plus solids), is
required in Eq. 2.1 because not all of the void space in a porous medium may be conducting liquid flow, such that \( n_e \) is less than the total porosity, \( n \), defined as the total volume of pore space defined as is used in lieu of \( n \) (i.e., \( n_e < n \)). The *advective mass flux*, \( J_a \), of a solute migrating through a porous medium due to advection, or hydraulically driven solute transport, then can be defined as follows:

\[
J_a = K_i c = n_e v_s c
\]  

(2.3)

where \( c \) = concentration of the solute in the liquid phase (solvent).

In contrast to advection, *diffusion* is the process whereby a solute is transported due to a gradient in the concentration of the solute. In this case, diffusion of the solute occurs relative to the solvent, and is independent of whether or not the solvent is moving. In this case, the *diffusive solute mass flux*, \( J_d \), is described by Fick’s first law, which for one-dimensional diffusion of a solute dissolved in a free (aqueous) solution (i.e., no porous media), can be written as follows:

\[
J_d = D_o i_c = -D_o \frac{\partial c}{\partial x}
\]

(2.4)

where \( D_o \) = the *aqueous-phase* or *free-solution* diffusion coefficient for the solute, and \( i_c \) = the concentration gradient. For solute diffusion in saturated porous media, such as saturated soil, Fick’s first law is modified as follows (Shackelford and Daniel, 1991):

\[
J_d = -n \tau_a D_o \frac{\partial c}{\partial x} = -nD^* \frac{\partial c}{\partial x}
\]

(2.5)
where $\tau_a$ = the apparent tortuosity factor as defined by Shackelford and Daniel (1991), and $D^*$ = the effective diffusion coefficient (= $\tau_aD_o$) for solute diffusion in porous media.

The dimensionless apparent tortuosity factor includes a geometric (or matrix) tortuosity factor, $\tau_g$, that takes into account the increased distance of transport and more tortuous pathways solutes travel while migrating through porous media, as well as any other factor, such as ion restriction, increased water viscosity adjacent to clay particles, etc.. The matrix tortuosity factor can be defined as follows (Shackelford and Daniel, 1991):

$$\tau_g = \left(\frac{L}{L_e}\right)^2 \tag{2.6}$$

where $L$ = the straight-line, macroscopic distance between two points defining the flow path, and $L_e$ = the actual, microscopic distance of transport between the same two points. Since $L_e > L$, $\tau_g < 1$ and $D^* < D_o$, such that diffusive mass transport in porous media is slower than that in aqueous solution. Values of the apparent tortuosity factor have been reported between 0.01 and 0.84 (Perkins and Johnston, 1963; Freeze and Cherry, 1979; Daniel and Shackelford, 1988; Shackelford, 1989; Shackelford and Daniel, 1991). A summary of values of $\tau_a$ is given in Table 2.1.

An additional solute mass transport process known as the mechanical dispersive flux, $J_m$, relates to the dispersion of a solute across an advective solute front due to variations in the seepage velocity during transport through porous media. At the microscopic scale, these variations have been attributed to three different effects (Fried, 1975; Bear, 1979; Freeze and
Cherry, 1979): (1) the variation in velocity across a single pore, from a value of zero adjacent to a particle comprising the porous medium to a maximum value at the center of the same pore; (2) variation in the sizes of pores that exist in a porous medium from location to location; and (3) the tortuous nature of the flow paths. At the macroscopic scale, mechanical dispersion is attributed to heterogeneity in the hydraulic conductivity of the porous medium (e.g., Gelhar et al. 1992). These effects are described in more detail by Fetter (1993) and Shackelford (1993).

The mechanical dispersive flux, \( J_m \), for one-dimensional transport is written in a form analogous to Fick’s first law, or:

\[
J_m = n_c D_m i_c = -n_c D_m \frac{\partial c}{\partial x}
\]  

(2.7)

where \( D_m \) = the mechanical dispersion coefficient. Although Eq. 2.7 is similar in form to Eq. 2.5, unlike \( D^* \), \( D_m \) is a function of the seepage velocity as follows (Freeze and Cherry, 1979):

\[
D_m = \alpha_L v_s^\beta
\]  

(2.8)

where \( \alpha_L \) = the longitudinal dispersivity of the porous media in the direction of transport, and \( \beta \) = empirically determined constant between 1 and 2.

The total solute mass flux, \( J \), is represented by the sum of three component fluxes, or:

\[
J = J_a + J_d + J_m
\]  

(2.9)
which, upon substituting Eqs. 2.3, 2.5, and 2.7 into Eq. 2.9, may be written as follows:

\[ J_m = n_e v_s c - n_e D^* \frac{\partial c}{\partial x} - n_e D_m \frac{\partial c}{\partial x} - n_e D_m \frac{\partial c}{\partial x} = n_e \left( v_s c - D_h \frac{\partial c}{\partial x} \right) \] (2.10)

where \( D_h \) = the hydrodynamic dispersion coefficient defined as follows:

\[ D_h = D^* + D_m = \tau_a D_o + \alpha_L v_s \] (2.11)

The hydrodynamic dispersion coefficient accounts for the combined influence of diffusion and mechanical dispersion on the overall dispersion of the solute during transport through porous media. However, mechanical dispersion tends to dominate when advection is the predominant transport process, such that \( D_m \gg D^* \) and \( D_h \approx D_m \), whereas the influence of diffusion increases with decreasing advection, such that the hydrodynamic dispersion coefficient approaches the effective diffusion coefficient in the limit as advection approaches zero (i.e., as \( v_s \to 0 \), \( D_h \to D^* \)).

### 2.2 Transient Transport

The governing equation for one-dimensional, transient transport of aqueous miscible chemical species (solutes) under steady-state flow is described by the following form of the advection-dispersion equation (Freeze and Cherry, 1979):
where $R_d = \text{retardation factor}$ for instantaneous, linear, and reversible sorption, and $c_r = \text{the resident concentration}$ or solute concentration in the pore water of the soil (van Genuchten and Parker, 1984). In addition to the aforementioned constraints inherent in the use of Eq. 2.12, the soil is assumed to be homogeneous, isotropic, and non-deformable, the liquid is assumed to be incompressible, and coupled flow processes (e.g., chemico-osmosis, thermo-osmosis, electro-osmosis) are assumed to be negligible.

The retardation factor, $R_d$, is a dimensionless parameter that represents attenuation capacity of a soil due to sorption of the solute to the solid soil matrix. In this case, sorption of the solute with the solid phase of the soil matrix is assumed to be linear, instantaneous, and reversible. A nonreactive (nonsorbing) solute has a retardation value of unity ($R_d = 1$), whereas a value of $R_d > 1$ describes an adsorbing (reactive) solute, resulting in slower chemical migration.

As previously noted, in the limit as $v_s \rightarrow 0$, $D_h \rightarrow D^*$, such that diffusion becomes the dominant transport process. In this case, Eq. 2.12 approaches the form of Fick’s second law governing transient diffusion of a reactive (sorbing) solute in porous media (Shackelford and Daniel, 1991), or:

$$R_d \frac{\partial c_r}{\partial t} = D^* \frac{\partial^2 c_r}{\partial x^2}$$  \hspace{1cm} (2.13)
2.3 Column Testing

Column testing has been used in agricultural applications to study the migration of nutrients to plants and soils, in chemical and process engineering to evaluate the breakthrough or elution of chemical species during migration through artificial or synthetically produced porous media (e.g., polymer resins), and in groundwater hydrology to evaluate the migration of chemical species through aquifers. In geoenvironmental engineering, there are three primary purposes for performing column tests (McCarty et al., 1981; Crooks and Quigley, 1984; Young et al. 1984; Acar and Haider, 1990; Shackelford and Daniel, 1991; Falatko and Novak, 1992; Shackelford, 1995b; Binley et al. 1996; Gusmão et al. 2004; Zhao et al. 2009; San Jose Martinez et al. 2010): (1) to measure the transport parameters \((D_h, R_d)\) of a contaminant (solute) through porous media; (2) to assess the effects of chemical and biological reactions on the fate of contaminants during transport through porous media; and (3) to verify/validate fate and transport theories and associated models used to predict contaminant migration through porous media.

A traditional approach for performing a column tests is based on a constant source concentration of one or more chemical species injected into a column of porous medium under the condition of steady-state seepage, as illustrated schematically in Fig. 2.1a. The procedure for conducting this traditional type of column test involves the following steps (Shackelford, 1994): (i) establishing steady-state flow of a solvent (e.g., water) through a column of a porous medium; (ii) continuously introducing a source chemical solution with known concentrations of chemical species \((c_o)\) as the influent, while still maintaining steady-state flow; and (iii) measuring the concentration \((c_e)\) of the same chemical species in the effluent as a function of time. The measured values of \(c_e\) are plotted as a function of time, \(t\), and the resulting curves of \(c_e\) versus \(t\) are known as breakthrough curves, or BTCs, as illustrated in Fig. 2.1b. The sigmoidal "S" shape
exhibited by the BTC is a result of dispersion of the solute during migration through the porous medium. Dispersion causes spreading of the solute both ahead and behind the advective front. Since a nonreactive (nonsorbing) solute ($R_d = 1$) arrives at the effluent end of the column earlier than a reactive (sorbing) solute ($R_d > 1$), the BTC of the nonreactive solute appears to the left of that for the reactive solute (see Fig. 2.1b). The solute mass flux and cumulative solute mass exiting the column also can be plotted as BTCs as illustrated schematically in Figs. 2.1c and 2.1d, respectively. In the case of Fig. 2.1d, the x-intercept of the cumulative mass BTC is equal to the value of $R_d$ (Shackelford 1995a).

2.4 Analytical Models for Evaluating Column Testing Data

In general, these models vary in terms of the initial and boundary conditions assumed to be relevant to the column testing, the mathematical approach used to solve Eq. 2.12 based on the initial and boundary conditions, (e.g., Laplace transforms versus Fourier series analyses), and the manner in which the fate processes expected to affect the chemical species during transport through the porous media (e.g., sorption, decay, etc.) are included in the governing equation. In terms of solutions to Eq. 2.12, Shackelford (1995b) evaluated four existing analytical models that differ both in terms of the boundary conditions and the mathematical approach used to obtain each of the analytical solutions. All four models were originally presented in the form of concentration based BTCs. Shackelford (1995b) also evaluated these four models in terms of mass flux BTCs and cumulative mass BTCs. All three forms of each model are presented in the following subsections.
2.4.1 Constant Source Concentration for Semi-Infinite Porous Medium

Probably the most commonly used model for analyzing the results of traditional column tests is the model based on a constant source concentration for a semi-infinite porous medium. This model will be referred to as Model 1. In this case, the boundary conditions can be written as follows (e.g., Freeze and Cherry, 1979):

\[
\begin{align*}
  c(0, t) &= c_0 \quad t \geq 0 \\
  c(\infty, t) &= 0 \quad t \geq 0
\end{align*}
\]

(2.14)

Application of these boundary conditions together with the condition that the porous medium is initially free of the solute of interest (i.e., \( c(x, 0) = 0 \)) to Eq. 2.12 for the case of a nonreactive (nonsorbing) solute (i.e., \( R_d = 1 \)) was first reported by Ogata and Banks (1961) as follows:

\[
\frac{c_r(x, t)}{c_0} = 0.5 \left\{ \text{erfc} \left( \frac{x-v_x t}{2\sqrt{D_h R_d t}} \right) + \exp \left( \frac{v_x x}{D_h} \right) \text{erfc} \left( \frac{x+v_x t}{2\sqrt{D_h t}} \right) \right\}
\]

(2.15)

where \( \text{erfc} = \) the complementary error function, which is defined as follows:

\[
\text{erfc} \beta = \frac{2}{\sqrt{\pi}} \int_{\beta}^{\infty} e^{-\xi^2} d\xi = \frac{2}{\sqrt{\pi}} \int_{\beta}^{\infty} \exp \left( -\xi^2 \right) d\xi
\]

(2.16)

where \( \beta = \) the argument of the complementary error function to be evaluated (e.g., see Abramowitz and Stegun, 1972). In general, the complementary error function of \( \beta \) ranges from 2
to 0 as $\beta$ ranges from $-\infty$ to $\infty$. For the case where $R_d > 1$, Eq. 2.15 may be written as follows (e.g., Lapidus and Amundson, 1952; van Genuchten and Parker, 1984; Shackelford, 1993):

$$
\frac{c_r(x,t)}{c_0} = 0.5 \left[ \text{erfc} \left( \frac{R_d x - v_s t}{2 \sqrt{D_h R_d t}} \right) + \exp \left( \frac{v_s x}{D_h} \right) \text{erfc} \left( \frac{R_d x + v_s t}{2 \sqrt{D_h R_d t}} \right) \right] \tag{2.17}
$$

The resident solute concentration at the end of the column, i.e., $c_r(L,t)$, often is taken as the effluent concentration, $c_e$. In this case, concentration-based BTCs such as illustrated in Fig. 2.1b often are presented in the form of a dimensionless or relative concentration, $RC (= c_e/c_o)$, versus dimensionless time, $T$ (i.e., $PVF = T$), where $T$ is defined as follows:

$$
T = \frac{v_s t}{L} \tag{2.18}
$$

In the case of constant seepage velocity, $T$ is equivalent to the pore volumes of solution flow through the column of porous medium.

Various studies have found that the evaluation of effluent concentration based on the collection of effluent concentrations recovered on a periodic basis then analyzed for chemical species is conceptually correct (Kreft and Zuber, 1978; Parker and van Genuchten, 1984; van Genuchten and Parker, 1984). However, the assumption of a semi-infinite porous medium conceptually is not valid. Also, the use of flux-averaged effluent concentration has been proposed as a more appropriate measure of effluent concentration than the resident solute concentration (Kreft and Zuber, 1978; Parker and van Genuchten, 1984; van Genuchten and
Parker, 1984). In this case, the flux-averaged effluent concentration is defined as the mass flux of the solute emanating from the soil column, \( J(L,t) \), relative to the liquid flux, or:

\[
c_e = \frac{J(L,t)}{v}
\]  

(2.19)

A flux-averaged relative concentration then can be defined as follows (e.g., Shackelford 1995b):

or:

\[
\frac{c_e}{c_o} = \frac{J(L,t)}{vc_o} = \frac{J(L,t)}{J_{ss}} = RF
\]  

(2.20)

where \( RF \) = the relative solute mass flux, and \( J_{ss} (= vc_o) \) is the solute mass flux at steady-state for the case of a constant-source concentration.

Analytical solutions based on resident concentrations, such as Eq. 2.17, can be converted to analytical solutions based on flux-based concentrations by determine the concentration gradient based on the resident concentration (i.e., \( \partial c_r / \partial x \)), substituting the resulting derivative into the expression for total solute flux (i.e., Eq. 2.10), evaluating the resulting expression at \( x = L \), and substituting this result into Eq. 2.20. With respect to Eq. 2.17, this procedure results in the following expression for the relative solute flux, \( RF \) (e.g., Shackelford, 1995):

\[
RF = 0.5 \left\{ \text{erf} \left( \frac{R_d^x - v_s t}{2\sqrt{D_h R_d t}} \right) + \frac{2}{\sqrt{\pi v_s^2 t / D_h R_d}} \text{erf} \left\{ -\left( \frac{R_d^x - v_s t}{2\sqrt{D_h R_d t}} \right)^2 \right\} \right\}
\]  

(2.21)
Thus, values of $RF$ evaluated at $x = L$ based on Eq. 2.21 can be used to determine the actual solute mass flux at $x = L$ versus time, $J(L,t)$, in accordance with Eq. 2.20.

A cumulative mass ratio, $CMR$, which represents the cumulative mass of solute in the effluent normalized with respect to the solute mass existing in the pore water of the porous medium after steady-state solute transport has been established can be defined as follows (Shackelford, 1995b):

$$
CMR = \sum_{V_p c_o}^{m} \frac{A}{nALc_o} = \frac{\int_0^t J(L,t) dt}{\int_0^t RF(t) dt} \quad (2.22)
$$

Thus, $CMR$ represents the integral of the relative solute mass flux normalized with respect to the elapsed column testing duration, $t$. With respect to Eq. 2.21, the resulting expression for $CMR$ is given as follows (Shackelford, 1995b):

$$
CMR = 0.5 \frac{D_h R_d}{v_s x} \left\{ \left( \frac{v_s^2 t}{D_h R_d} - \frac{v_s L}{D_h} + 1 \right) \text{erfc} \left( \frac{R_d x - v_s t}{2 \sqrt{D_h R_d t}} \right) - \exp \left( \frac{v_s L}{D_h} \right) \text{erfc} \left( \frac{R_d x + v_s t}{2 \sqrt{D_h R_d t}} \right) \right\} \quad (2.23)
$$
2.4.2 Conservation of Mass Flux for Semi-Infinite Porous Medium

Lindstrom et al. (1967) presented an alternative analytical solution for the case of a semi-infinite porous medium whereby, instead of a constant-source concentration upper boundary condition, they imposed the condition of conservation of solute mass flux across the upper boundary. This model will be referred to as Model 2. Their boundary conditions can be written as follows:

\[
\begin{align*}
-D_h \frac{\partial c}{\partial x} + v_x c &= v c_o |_{x=0^+} ; \quad t \geq 0 \\
\frac{\partial c}{\partial x} |_{x=h} &= 0 ; \quad t \geq 0
\end{align*}
\]  

(2.24)

where the initial concentration of the solute in the reservoir, \(c_o\), is constant, and the solute in the influent reservoir is well mixed such that the flux entering the column is due to advection only. Application of these boundary conditions to Eq. 2.12 results in the following analytical solution based on resident, or volume averaged, concentrations (Lindstrom et al., 1967; Gershon and Nir, 1969; van Genuchten and Parker, 1984):

\[
\frac{c_r(x,t)}{c_0} = RC.2 = 0.5 \left\{ \text{erfc} \left( \frac{R_d x - v t}{2 \sqrt{D_h R_d t}} \right) + 2 \sqrt{\frac{v^2 t}{\pi D_h R_d}} \exp \left( \frac{R_d x - v t^2}{4 D_h R_d t} \right) \right\} - \left( 1 + \frac{v x}{D_h} + \frac{v^2 t}{D_h R_d} \right) \exp \left( \frac{v x}{D_h} \right) \text{erfc} \left( \frac{R_d x + v t}{2 \sqrt{D_h R_d t}} \right)
\]

(2.25)
The corresponding expressions for relative flux and cumulative mass ratio based on Eq. 2.25 are given as follows (e.g., Shackelford, 1995b):

\[
RF.2 = 0.5 \left\{ \text{erfc} \left( \frac{R_d x - v_s t}{\sqrt{2D_h R_d t}} \right) + \exp \left( \frac{v_s x}{D_h} \right) \text{erfc} \left( \frac{R_d x - v_s t}{2\sqrt{D_h R_d t}} \right) \right\} \tag{2.26}
\]

and

\[
CMR.2 = 0.5 \frac{D_h R_d}{v_s x} \left\{ \left( \frac{v_s^2 t}{D_h R_d} - \frac{v_s L}{D_h} \right) \text{erfc} \left( \frac{R_d x - v_s t}{2\sqrt{D_h R_d t}} \right) \right. \\
+ \left. \left( \frac{v_s^2 t}{D_h R_d} + \frac{v_s L}{D_h} \right) \exp \left( \frac{v_s L}{D_h} \right) \text{erfc} \left( \frac{R_d x + v_s t}{2\sqrt{D_h R_d t}} \right) \right\} \tag{2.27}
\]

### 2.4.3 Constant Source Concentration for Finite Porous Medium

Cleary and Adrian (1973) presented an analytical solution for a finite porous medium with a constant source concentration. This model will be referred to as Model 3. These boundary conditions can be written as follows:

\[
c(0, t) = c_0 \quad t \geq 0 \\
c(L, t) = 0 \quad t \geq 0 \tag{2.28}
\]
Application of these boundary conditions to Eq. 2.12 results in the following analytical solution based on resident, or volume averaged, concentrations (Cleary and Adrian, 1973; van Genuchten and Parker, 1984):

\[
\frac{c_r(x,t)}{c_0} = RC.3 = 1 - \sum_{m=1}^{\infty} \frac{2\alpha_m \sin \left( \frac{\alpha_m x}{L} \right) \exp \left( \frac{v_s x}{2D_h} - \frac{v^2 t}{4D_h R_d} - \frac{\alpha_m^2 D_h t}{L^2 R_d} \right)}{\alpha_m^2 + \left( \frac{v_s L}{2D_h} \right)^2 + \frac{v_s L}{2D_h}}
\] (2.29)

where the eigenvalues \( \alpha_m \) are the positive roots of the following expression:

\[
\alpha_m \cot \alpha_m + \frac{v_s L}{D_h} = 0
\] (2.30)

The corresponding expressions for relative flux and cumulative mass ratio based on Eqs. 2.29 and 2.30 are given as follows (e.g., Shackelford, 1995b):

\[
RF.3 = 1 - \sum_{m=1}^{\infty} \frac{\alpha_m \left( \sin \left( \frac{\alpha_m x}{L} \right) - \frac{2\alpha_m D_h}{v_s x} \cos \left( \frac{\alpha_m x}{L} \right) \right) \exp \left( \frac{v_s x}{2D_h} - \frac{v^2 t}{4D_h R_d} - \frac{\alpha_m^2 D_h t}{L^2 R_d} \right)}{\alpha_m^2 + \left( \frac{v_s L}{2D_h} \right)^2 + \frac{v_s L}{2D_h}}
\] (2.31)

and
2.4.4 Conservation of Mass Flux for Finite Porous Medium

Brenner (1962) presented an analytical solution to Eq. 2.12 for a finite porous medium and conservation of solute mass flux as the upper boundary condition. This model will be referred to as Model 4. These boundary conditions can be written as follows as follows:

\[
\begin{align*}
\left(-D_h \frac{\partial c}{\partial x} + v_x c\right)_{x=0^-} &= vc_o \mid_{x=0^+} ; \quad t \geq 0 \\
\frac{\partial c}{\partial x} \mathbf{u}, t &= 0 ; \quad t \geq 0
\end{align*}
\]

(2.33)

Application of these boundary conditions to Eq. 2.12 results in the following analytical solution based on resident, or volume averaged, concentrations (Brenner, 1962; van Genuchten and Parker, 1984):

\[
c_l(x,t) = RC.1 = 1 - \sum_{m=1}^{\infty} \left[ \frac{2v_x L}{D_h} \beta_m \cos \left( \frac{\beta_m x}{L} \right) + \frac{v_x L}{D_h} \sin \left( \frac{\beta_m x}{L} \right) \right] \exp \left[ \frac{v_x x}{2D_h} - \frac{v_x^2 t}{4D_h R_d} - \frac{\beta_m^2 D_h t}{L^2 R_d} \right]
\]

(2.34)

where the eigenvalues \( \beta_m \) are the positive roots of the following expression:
\[ \beta_m \cot \beta_m = \frac{\beta_m^2 D}{vL} + \frac{v_s L}{4D_h} = 0 \]  

(2.35)

The corresponding expressions for relative flux and cumulative mass ratio based on Eqs. 2.34 and 2.35 are given as follows (e.g., Shackelford 1995b):

\[ RF,4 = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin \left( \frac{\beta_m x}{L} \right) \exp \left( \frac{v_s x}{2D_h} - \frac{v_s^2 t}{4D_h R_d} - \frac{\beta_m^2 D_h t}{L^2 R_d} \right)}{\beta_m^2 + \left( \frac{v_s L}{2D_h} \right)^2 + \frac{v_s L}{D_h}} \]  

(2.36)

and

\[ CMR,4 = \frac{R_d D_h}{v_s L} \left[ \frac{v_s^2 t}{D_h R_d} \right] + 8 \sum_{m=1}^{\infty} \frac{2\beta_m \sin \left( \frac{\beta_m x}{L} \right) \exp \left( \frac{v_s x}{2D_h} - \frac{v_s^2 t}{4D_h R_d} - \frac{\beta_m^2 D_h t}{L^2 R_d} \right)}{\beta_m^2 + \left( \frac{v_s L}{2D_h} \right)^2 + \frac{v_s L}{D_h}} \left[ 1 + \left( \frac{2\beta_m D_h}{v_s L} \right)^2 \right] \]  

(2.37)

### 2.4.5 Summary of Analytical Models for Breakthrough Curves from Column Tests

A summary of the concentration-based models (RC.1, RC.2, RC.3, and RC.4) for one-dimensional advection-dispersion with sorption (from Shackelford, 1995b) is presented in Table 2.2. Dimensionless forms of concentration-based models (RC.1, RC.2, RC.3, and RC.4)
are presented in Table 2.3 in terms of a dimensionless column Péclet number, $P_L$, and dimensionless reactive time, $T_r$, where.

$$P_L = \frac{v}{D}$$ (2.38)

$$T_r = \frac{T}{R_d}$$ (2.39)

where $T =$ pore volume of flow as given by Eq. 2.18.

The four theoretical models are summarized in Table 2.4 for $RC$, $RF$, and $CMR$. The dimensionless form of the four theoretical models are summarized in Table 25.
Table 2.1 Representative apparent tortuosity factors from the literature

<table>
<thead>
<tr>
<th>Soil(s)</th>
<th>Saturated or unsaturated</th>
<th>$\tau_a$ Values$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) $^{35}\text{Cl}^-$ Tracer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite: sand mixtures</td>
<td>Saturated</td>
<td>0.59-0.84</td>
<td>Gillham et al. (1984)</td>
</tr>
<tr>
<td>50% sand: bentonite mixture</td>
<td>Saturated</td>
<td>0.08-0.12</td>
<td>Gillham et al. (1985)</td>
</tr>
<tr>
<td>Bentonite: sand mixtures</td>
<td>Saturated</td>
<td>0.04-0.49</td>
<td>Johnston et al. (1984)</td>
</tr>
<tr>
<td>(b) $\text{Cl}^-$ Tracer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandy loam</td>
<td>Unsaturated</td>
<td>0.21-0.35$^a$</td>
<td>Barraclough and Nye (1979)</td>
</tr>
<tr>
<td>Sand</td>
<td>Unsaturated</td>
<td>0.025-0.29$^a$</td>
<td>Porter et al. (1960)</td>
</tr>
<tr>
<td>Silty clay loam</td>
<td>Unsaturated</td>
<td>0.064-0.26$^a$</td>
<td>Porter et al. (1960)</td>
</tr>
<tr>
<td>Clay</td>
<td>Unsaturated</td>
<td>0.091-0.28$^a$</td>
<td>Porter et al. (1960)</td>
</tr>
<tr>
<td>Silt loam</td>
<td>Unsaturated</td>
<td>0.031-0.57$^a$</td>
<td>Warncke and Barber (1972)</td>
</tr>
<tr>
<td>Sandstone</td>
<td>Saturated</td>
<td>0.099</td>
<td>Feenstra et al. (1984)</td>
</tr>
<tr>
<td>Shale</td>
<td>Saturated</td>
<td>0.010</td>
<td>Barone et al. (1990)</td>
</tr>
<tr>
<td>Silty clay loam; sandy loam</td>
<td>Saturated</td>
<td>0.08-0.22$^a$</td>
<td>Barraclough and Tinker (1981)</td>
</tr>
<tr>
<td>Silty clay</td>
<td>Saturated</td>
<td>0.13-0.30$^a$</td>
<td>Crooks and Quigley (1984)</td>
</tr>
<tr>
<td>Clay</td>
<td>Saturated</td>
<td>0.20-0.33</td>
<td>Johnston et al. (1981)</td>
</tr>
<tr>
<td>Clay</td>
<td>Saturated</td>
<td>0.28-0.31$^a$</td>
<td>Rowe et al. (1988)</td>
</tr>
<tr>
<td>(c) $\text{Br}^-$ Tracer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silty clay loam; sandy loam</td>
<td>Saturated</td>
<td>0.19-0.30$^a$</td>
<td>Barraclough and Tinker (1981)</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>Saturated</td>
<td>0.25-0.35$^a$</td>
<td>Barraclough and Tinker (1982)</td>
</tr>
<tr>
<td>(d) $^3\text{H}$ Tracer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite: sand mixtures</td>
<td>Saturated</td>
<td>0.33-0.70</td>
<td>Gillham et al. (1984)</td>
</tr>
<tr>
<td>Bentonite: sand mixtures</td>
<td>Saturated</td>
<td>0.01-0.22</td>
<td>Johnston et al. (1984)</td>
</tr>
<tr>
<td>(e) $\Gamma^-$ Tracer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Granite</td>
<td>Saturated</td>
<td>0.06</td>
<td>Skagius and Neretnieks (1984)</td>
</tr>
</tbody>
</table>

$^a$ Values were calculated using the appropriate $D_o$ for the representative ions at infinite dilution in water at $25^\circ\text{C}$ and $D^*$ value taken from reference.

$^b$ Calculated using the appropriate $D_o$ at $10^\circ\text{C}$ and $D^*$ value taken from reference.
Table 2.2 Concentration-based models for one-dimensional advection-dispersion with sorption (from Shackelford 1995b)

| Model Designation | Upper Boundary Condition | Lower Boundary Condition | Concentration Models\(^{(1)}\)  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RC.1</td>
<td>(c_r(0,t) = c_o) (\frac{\partial c_r}{\partial x}(\infty,t) = 0)</td>
<td>(\frac{\partial c_r}{\partial x}(\infty,t) = 0)</td>
<td>(\frac{c_r(x,t)}{c_0} = 0.5 \left{ \text{erf}\left( \frac{R_d x-vt}{2\sqrt{D_h R_d t}} \right) + \exp\left( \frac{v x}{D_h} \right) \text{erf}\left( \frac{R_d x+vt}{2\sqrt{D_h R_d t}} \right) \right} )</td>
<td>Lapidus and Amundson (1952)</td>
</tr>
<tr>
<td>RC.2</td>
<td>(v c_r - D_h \frac{\partial c_r}{\partial x}) (t = 0) (\frac{\partial c_r}{\partial x}(\infty,t) = 0)</td>
<td>(\frac{\partial c_r}{\partial x}(\infty,t) = 0)</td>
<td>(\frac{c_r(x,t)}{c_0} = 0.5 \left{ \text{erf}\left( \frac{R_d x-vt}{2\sqrt{D_h R_d t}} \right) + 2 \frac{v^2 t}{\pi D_h R_d} \exp\left( -\frac{R_d x-vt^2}{4D_h R_d t} \right) \right} )</td>
<td>Lindstrom et al. (1967)</td>
</tr>
<tr>
<td>RC.3</td>
<td>(c_r(0,t) = c_o) (\frac{\partial c_r}{\partial x}(L,t) = 0)</td>
<td>(\frac{\partial c_r}{\partial x}(L,t) = 0)</td>
<td>(\frac{c_r(x,t)}{c_0} = 1 - \sum_{m=1}^{\infty} \frac{2\alpha_m \sin\left( \frac{\alpha_m x}{L} \right) \exp\left( \frac{v x}{2D_h} - \frac{v^2 t}{4D_h R_d} - \frac{\alpha_m^2 D_t}{L^2 R_d} \right)}{\alpha_m^2 + \left( \frac{v L}{2D_h} \right)^2 + \frac{v L}{D_h}} ) )</td>
<td>Cleary and Adrian (1973)</td>
</tr>
<tr>
<td>RC.4</td>
<td>(v c_r - D_h \frac{\partial c_r}{\partial x}) (t = 0) (\frac{\partial c_r}{\partial x}(L,t) = 0)</td>
<td>(\frac{\partial c_r}{\partial x}(L,t) = 0)</td>
<td>(\frac{c_r(x,t)}{c_0} = 1 - \sum_{m=1}^{\infty} \frac{2\nu L \beta_m \left[ \beta_m \cos\left( \frac{\beta_m x}{L} \right) - \frac{v L}{2D_h} \sin\left( \frac{\beta_m x}{L} \right) \right] \exp\left( \frac{v x}{2D_h} - \frac{v^2 t}{4D_h R_d} - \frac{\beta_m^2 D_t}{L^2 R_d} \right)}{\beta_m^2 + \left( \frac{v L}{2D_h} \right)^2 + \frac{v L}{D_h} \beta_m^2 + \left( \frac{v L}{2D_h} \right)^2} ) )</td>
<td>Brenner (1962)</td>
</tr>
</tbody>
</table>

\(1\) \(T = \frac{v x t}{L} ; \ T_r = \frac{T}{R_d} ; \ P_L = \frac{v L}{D_h} ; \)
Table 2.3 Dimensionless forms of concentration-based models for one-dimensional advection-dispersion

<table>
<thead>
<tr>
<th>Model Designation</th>
<th>Concentration Models$^{(1)}$ [for (c(L,t) = 0)]</th>
</tr>
</thead>
</table>
| RC.1              | \[
\frac{c_r}{c_0}(L,t) = 0.5 \left\{ \text{erfc} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + \exp \left( \frac{L}{T_r} \text{erfc} \left( \frac{1+T_r}{2\sqrt{T_r/P_L}} \right) \right) \right\} 
\] |
| RC.2              | \[
\frac{c_r}{c_0}(x,t) = 0.5 \left\{ \text{erfc} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + 2\sqrt{\frac{T_r P_L}{\pi}} \exp \left( -\frac{L^2}{4T_r/P_L} \right) 
- \left( \frac{L}{T_r} \text{erfc} \left( \frac{1+T_r}{2\sqrt{T_r/P_L}} \right) \right) \right\} 
\] |
| RC.3              | \[
\frac{c_r}{c_0}(L,t) = 1 - \sum_{m=1}^{\infty} \frac{2\alpha_m \sin \alpha_m \exp \left( \frac{P_L - T_r P_L}{2} - \frac{\alpha_m^2 T_r}{P_L} \right)}{\left( \alpha_m^2 + \frac{P_L^2}{2} + \frac{P_L}{2} \right)} 
\] where eigenvalues \(\alpha_m\) are the positive roots of \(\alpha_m \cot \alpha_m + P_L = 0\) |
| RC.4              | \[
\frac{c_r}{c_0}(x,t) = 1 - \sum_{m=1}^{\infty} 2P_L \beta_m \left[ \cos \beta_m \exp \left( \frac{P_L - T_r P_L}{2} - \frac{\beta_m^2 T_r}{P_L} \right) \right] \frac{\left( \beta_m^2 + \frac{P_L^2}{2} + P_L \right)}{\left( \beta_m^2 + \frac{P_L^2}{2} \right)} 
\] where eigenvalues \(\beta_m\) are the positive roots of \(\beta_m \cot \beta_m - \frac{\beta_m^2}{P_L} + \frac{P_L}{4} = 0\) |

(1) \(T = \frac{v_s f}{L}; \ T_r = \frac{T}{R_d}; \ P_L = \frac{vL}{D_h}\)
Table-2.4  Summary of Theoretical Equations

<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
</table>
| \(c_r(0,t) = c_o\) \(\frac{\partial c_r}{\partial x}(\infty,t) = 0\) | \(c_o\) | RC.1 | \[
\frac{c_r(x,t)}{c_o} = 0.5 \left\{ \text{erf} \left( \frac{R_d x - v_r t}{2 \sqrt{D_h R_d t}} \right) + \exp \left( \frac{v_r x}{D_h} \right) \text{erf} \left( \frac{R_d x + v_r t}{2 \sqrt{D_h R_d t}} \right) \right\}
\]
| | | RF.1 | \[
RF = 0.5 \left\{ \text{erf} \left( \frac{R_d x - v_r t}{2 \sqrt{D_h R_d t}} \right) + \frac{2}{\pi \sqrt{v_r^2 t/v_D R_d}} \text{erf} \left( -\frac{R_d x - v_r t}{2 \sqrt{D_h R_d t}} \right) \right\}
\]
| | | CMR.1 | \[
CMR = 0.5 \frac{D_h R_d}{v_r x} \left\{ \frac{v_r^2 t}{D_h R_d} - \frac{v_r L}{D_h} + 1 \right\} \text{erf} \left( \frac{R_d x - v_r t}{2 \sqrt{D_h R_d t}} \right) - \exp \left( \frac{v_r L}{D_h} \right) \text{erf} \left( \frac{R_d x + v_r t}{2 \sqrt{D_h R_d t}} \right) \right\}
+ 2 \frac{v_r^2 t}{\pi D_h R_d} \text{erf} \left( -\frac{R_d x - v_r t}{2 \sqrt{D_h R_d t}} \right)\]

(1) \(T = \frac{v_r L}{L} ; T_r = \frac{T}{R_d} ; P_L = \frac{v r L}{D_h}\)
Table-2.4  Summary of Theoretical Equations Continued

<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
</table>
| \( \left( \frac{v_c R}{D_h} - \frac{D_h}{\partial x} \frac{\partial c_f}{\partial x} \right) \big|_{x=0} = v_c c_0 \) | \( \frac{\partial c_f}{\partial x} \big|_{x=0} = 0 \) | RC.2 | \[
\begin{align*}
\frac{c_f}{c_0} (x,t) &= 0.5 \left\{ \text{erf} \left( \frac{R_d x - v_i t}{2 \sqrt{D_h R_d}} \right) + 2 \frac{v_i^2 t}{\pi D_h R_d} \exp \left( - \frac{R_d x - v_i t}{4 D_h R_d} \right) \\
& \quad - \left( 1 + \frac{v_i x}{D_h} + \frac{v_i^2 t}{D_h R_d} \right) \exp \left( \frac{v_i x}{D_h} \right) \text{erf} \left( \frac{R_d x + v_i t}{2 \sqrt{D_h R_d}} \right) \right\}
\end{align*}
\] |
| | | RF.2 | \[
\begin{align*}
RF &= 0.5 \left\{ \text{erf} \left( \frac{R_d x - v_i t}{2 \sqrt{D_h R_d}} \right) + \exp \left( \frac{v_i x}{D_h} \right) \text{erf} \left( - \frac{R_d x - v_i t}{2 \sqrt{D_h R_d}} \right) \right\}
\end{align*}
\] |
| | | CMR.2 | \[
\begin{align*}
CMR &= 0.5 \frac{D_h R_d}{v_i x} \left\{ \left( \frac{v_i^2 t}{D_h R_d} - \frac{v_i L}{D_h} \right) \text{erf} \left( \frac{R_d x - v_i t}{2 \sqrt{D_h R_d}} \right) \right. \\
& \quad + \left( \frac{v_i^2 t}{D_h R_d} + \frac{v_i L}{D_h} \right) \exp \left( \frac{v_i L}{D_h} \right) \text{erf} \left( \frac{R_d x + v_i t}{2 \sqrt{D_h R_d}} \right) \left. \right\}
\end{align*}
\] |

(1) \( T = \frac{v_i t}{L} \); \( T_c = \frac{T}{R_d} \); \( P_L = \frac{v i L}{D_h} \)
Table 2.4 Summary of Theoretical Equations Continued

<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_r(0,t) = c_o$</td>
<td>$rac{\partial c_r}{\partial x}(L,t) = 0$</td>
<td>RC.3</td>
<td>$\frac{c_L}{c_0}(x,t) = 1 - \sum_{m=1}^{\infty} \frac{2\alpha_m \sin \left( \frac{\alpha_m x}{L} \right) \exp \left( \frac{v_x x}{2D_h} - \frac{v_x^2 t}{4D_h R_d} - \frac{\alpha_m^2 D_h t}{L^2 R_d} \right)}{\alpha_m^2 + \left( \frac{v_x L}{2D_h} \right)^2 + \frac{v_x L}{2D_h}}$</td>
</tr>
<tr>
<td>$\frac{\partial c_r}{\partial x}(L,t) = 0$</td>
<td>$RF = 1 - \sum_{m=1}^{\infty} \frac{\alpha_m \sin \left( \frac{\alpha_m x}{L} \right) - 2\alpha_m D_h \cos \left( \frac{\alpha_m x}{L} \right)}{v_x x} \exp \left( \frac{v_x x}{2D_h} - \frac{v_x^2 t}{4D_h R_d} - \frac{\alpha_m^2 D_h t}{L^2 R_d} \right) \left( \frac{\alpha_m^2 + \left( \frac{v_x L}{2D_h} \right)^2 + \frac{v_x L}{2D_h}}{1 + \left( \frac{2\alpha_m D_h}{v_x L} \right)^2} \right)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_r(0,t) = c_o$</td>
<td>$CMR = \frac{R_d D_h}{v_x L}$</td>
<td>CMR.3</td>
<td>$\frac{v_x^2 t}{D_h R_d} + \sum_{m=1}^{\infty} \frac{\alpha_m \sin \left( \frac{\alpha_m x}{L} \right) - 2\alpha_m D_h \cos \left( \frac{\alpha_m x}{L} \right)}{v_x x} \exp \left( \frac{v_x x}{2D_h} - \frac{v_x^2 t}{4D_h R_d} - \frac{\alpha_m^2 D_h t}{L^2 R_d} \right) \left( \frac{\alpha_m^2 + \left( \frac{v_x L}{2D_h} \right)^2 + \frac{v_x L}{2D_h}}{1 + \left( \frac{2\alpha_m D_h}{v_x L} \right)^2} \right)$</td>
</tr>
</tbody>
</table>

(1) $T = \frac{v_x L}{L} ; \ T_r = \frac{T}{R_d} ; \ P_L = \frac{vL}{D_h}$
<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(v_c - D_h \frac{\partial c_c}{\partial x})</td>
<td>_{x=0}$</td>
<td>$\frac{\partial c_s}{\partial x}(L,t)=0$</td>
<td>$RC.4$</td>
</tr>
<tr>
<td>$= v_c$</td>
<td></td>
<td></td>
<td>where eigenvalues $\beta_m$ are the positive roots of $\beta_m \cot \beta_m - \frac{\beta_m^2 D}{v_c L} + \frac{v_c L}{4D_h} = 0$</td>
</tr>
<tr>
<td>$\frac{v_c L}{D_h}$</td>
<td>$RF.4$</td>
<td>$RF = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin \left( \frac{\beta_m x}{L} \right) \exp \left[ \frac{v_s L - \frac{v_s^2 t}{4D_h R_d} - \frac{\beta_m^2 D_h t}{L^2 R_d}}{2D_h} \right]}{\beta_m^2 + \frac{v_s L}{2D_h} + \frac{v_c L}{D_h}}$</td>
<td></td>
</tr>
<tr>
<td>$= v_s \frac{L}{R_d}$</td>
<td></td>
<td></td>
<td>where eigenvalues $\beta_m$ are the positive roots of $\beta_m \cot \beta_m - \frac{\beta_m^2 D}{v_s L} + \frac{v_s L}{4D_h} = 0$</td>
</tr>
<tr>
<td>CMR.4</td>
<td>$CMR = \frac{R_d D_h}{v_s L} \left[ \frac{v_s^2 t}{D_h R_d} + 8 \sum_{m=1}^{\infty} \frac{2\beta_m \sin \left( \frac{\beta_m x}{L} \right) \exp \left[ \frac{v_s L - \frac{v_s^2 t}{4D_h R_d} - \frac{\beta_m^2 D_h t}{L^2 R_d}}{2D_h} \right]}{\beta_m^2 + \frac{v_s L}{2D_h} + \frac{v_c L}{D_h}} \left[ 1 + \frac{2\beta_m D_h}{v_s L} \right] \right]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>where eigenvalues $\beta_m$ are the positive roots of $\beta_m \cot \beta_m - \frac{\beta_m^2 D}{v_s L} + \frac{v_s L}{4D_h} = 0$</td>
</tr>
</tbody>
</table>

(1) $T = \frac{v_s L}{L}$; $T_r = \frac{T}{R_d}$; $P_L = \frac{vL}{D_h}$
Table 2.5 Summary of Equations in Dimensionless Form

<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_f(0,t) = c_o$</td>
<td>$\frac{\partial c_L}{\partial x}(\infty, t) = 0$</td>
<td>RC.1</td>
<td>[ \frac{c_r(L,t)}{c_o} = 0.5 \left{ \text{erf} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + \text{exp} \left( \frac{1}{2\sqrt{T_r/P_L}} \right) \right} ]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RF.1</td>
<td>[ RF = 0.5 \left{ \text{erf} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + \frac{2}{\sqrt{\pi T_r P_L}} \exp \left( -\frac{T_r^{-2}}{2\sqrt{T_r/P_L}} \right) \right} ]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CMR.1</td>
<td>[ CMR = \frac{0.5 R_d}{P_L} \left{ \phi_L T_r - P_L + 1 \text{erf} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + \text{exp} \left( \frac{1}{2\sqrt{T_r/P_L}} \right) \right} ]</td>
</tr>
</tbody>
</table>

(1) $T = \frac{v_s L}{L} ; \ T_r = \frac{T}{R_d} ; \ P_L = \frac{vL}{D_b}$
Table 2.5 Summary of Equations in Dimensionless Form Continued

<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_c, D_h \frac{\partial c_r}{\partial x} )</td>
<td>( \frac{\partial c_r}{\partial x}(\infty,t) = 0 )</td>
<td>RC.2</td>
<td>( c_r(0,t) = \frac{0.5 \left( \text{erf} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + 2 \sqrt{T_r/P_L} \exp \left( \frac{1}{4T_r/P_L} \right) \right)}{c_0} ) - ( \frac{c_r}{c_0} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RF.2</td>
<td>( RF = \frac{0.5 \left( \text{erf} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) + \exp \left( \frac{1}{2\sqrt{T_r/P_L}} \right) \right)}{\text{erfc} \left( \frac{1}{2\sqrt{T_r/P_L}} \right)} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CMR.2</td>
<td>( \text{CMR} = \frac{0.5 R_d}{P_L} \left( \Phi_r P_L - P_L \text{erfc} \left( \frac{1-T_r}{2\sqrt{T_r/P_L}} \right) \right) + \Phi_r P_L + P_L \text{erfc} \left( \frac{1+T_r}{2\sqrt{T_r/P_L}} \right) )</td>
</tr>
</tbody>
</table>

(1) \( T = \frac{v_d t}{L} \); \( T_r = \frac{T}{R_d} \); \( P_L = \frac{v L}{D_h} \)
Table 2.5 Summary of Equations in Dimensionless Form Continued

<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
</table>
|                                   |                                    | RC.3              | \[
\frac{c_r (L, t)}{c_o} = 1 - \sum_{m=1}^{\infty} \frac{2\alpha_m \sin \phi_m \exp \left( \frac{P_L}{2} - \frac{T_r P_L}{4} - \frac{\alpha_m^2 T_r}{P_L} \right)}{\left( \alpha_m + \left( \frac{P_L}{2} \right)^2 + \frac{P_L}{2} \right)}
\] where eigenvalues $\alpha_m$ are the positive roots of $\alpha_m \cot \alpha_m + P_L = 0$
| $c_r(0,t) = c_o$                 | $\frac{\partial c_r}{\partial x} (L, t) = 0$ | RF.3              | \[
RF = \left\{ 1 - \sum_{m=1}^{\infty} \frac{\alpha_m \left( \sin \phi_m - \frac{2\alpha_m \cos \phi_m}{P_L} \right) \exp \left( \frac{P_L}{2} - \frac{T_r P_L}{4} - \frac{\alpha_m^2 T_r}{P_L} \right)}{\left( \alpha_m + \left( \frac{P_L}{2} \right)^2 + \frac{P_L}{2} \right)} \right\}
\] where eigenvalues $\alpha_m$ are the positive roots of $\alpha_m \cot \alpha_m + P_L = 0$
|                                   |                                    | CMR.3             | \[
CMR = \frac{R_d}{P_L} \left\{ P_L T_r + 4 \sum_{m=1}^{\infty} \frac{\alpha_m \left( \sin \phi_m - \frac{2\alpha_m \cos \phi_m}{P_L} \right) \exp \left( \frac{P_L}{2} - \frac{T_r P_L}{4} - \frac{\alpha_m^2 T_r}{P_L} \right)}{\left( \alpha_m + \left( \frac{P_L}{2} \right)^2 + \frac{P_L}{2} \right) \left( 1 + \frac{2\alpha_m}{P_L} \right)} \right\}
\] where eigenvalues $\alpha_m$ are the positive roots of $\alpha_m \cot \alpha_m + P_L = 0$

(1) $T = \frac{\nu L}{L}$; $T_r = \frac{T}{R_d}$; $P_L = \frac{\nu L}{D_b}$
<table>
<thead>
<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
</tr>
</thead>
</table>
|                                   |                                    | RC.4             | \[
\frac{c_r}{c_0} (L,t) = 1 - \sum_{m=1}^{\infty} \frac{2P_L \beta_m \left[ \beta_m \cos \Phi_m + \frac{P_L}{2} \sin \Phi_m \right]}{\beta_m^2 + \left(\frac{P_L}{2}\right)^2 + P_L} \exp \left(\frac{P_L}{2} - \frac{T_r P_L}{4} - \frac{\beta_m^2 T_r}{P_L}\right)
\] |
|                                   |                                    | RF.4             | \[
RF = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin \Phi_m \exp \left(\frac{P_L}{2} - \frac{T_r P_L}{4} - \frac{\beta_m^2 T_r}{P_L}\right)}{\beta_m^2 + \left(\frac{P_L}{2}\right)^2 + P_L}
\] |
| \[
\left( v c_r - D_b \frac{\partial c_r}{\partial x} \right)_{t=0} = v c_o
\] | \[
\frac{\partial c_r}{\partial x} (L,t) = 0
\] | CMR.4             | \[
CMR = \frac{R_d}{P_L} \left\{ P_L T_r + 8 \sum_{m=1}^{\infty} \frac{2\beta_m \sin \Phi_m \exp \left(\frac{P_L}{2} - \frac{T_r P_L}{4} - \frac{\beta_m^2 T_r}{P_L}\right)}{\beta_m^2 + \left(\frac{P_L}{2}\right)^2 + P_L} \right\}^{1 + \left(\frac{2\beta_m^2}{P_L}\right)^2}
\] |

where eigenvalues $\beta_m$ are the positive roots of $\beta_m \cot \beta_m - \frac{\beta_m^2}{P_L} + \frac{P_L}{4} = 0$

(1) $T = \frac{\nu d}{L}$; $T = \frac{T}{R_d}$; $P_L = \frac{\nu L}{D_b}$
Figure 2.1 Schematic illustration of a constant-source column test with a constant seepage velocity: (a) column test set up; (b) concentration breakthrough curves (BTC); (c) solute mass flux BTCs; (d) cumulative mass BTCs. \( c_s \) = source concentration; \( c_e \) = effluent concentration; \( v_s \) = seepage velocity; \( v \) = Darcy velocity; \( R_d \) = retardation factor; \( J_{ss} \) = steady-state solute mass flux
CHAPTER 3 - RESULTS AND DISCUSSION

3.1 Computer Programs

The objective of this study was to program the 12 analytical models summarized in Table 2.3 in the form of Excel (Version 14.0.4763.1000, 2010, Microsoft Corporation, Redmond, WA) and/or Matlab (Version 7.11.0.584, R2010b, MathWorks, Natick, MA) for the purpose of facilitating the use of these models. Models RC.1, RF.1, CMR.1, RC.2, RF.2, and CMR.2 were programmed in both Excel and Matlab. However, because Excel does not have the capability to solve for the \( \alpha_m \) (Eq.2.30) and \( \beta_m \) (Eq.2.35) roots required for models RC.3, RF.3, CMR.3 and models RC.4, RF.4, and CMR.4, respectively, these models were programmed only in Matlab. Following programming of the models, a series of simulations was performed with each model in order to validate the accuracy of the models relative to the simulations results previously reported by Shackelford (1995b). Additional simulations then were performed to illustrate the general usage of the programmed models.

3.2 Model Validation

The relative concentration, relative flux, and cumulative mass models were evaluated for a non-reactive solute \( (R_d = 1) \) and varying column Péclet numbers, \( P_L \), of 1, 5, 20, and 50. This range of \( P_L \) represents the transport of aqueous miscible solutes (e.g., contaminants) through relatively short distances (e.g., van Geuchten and Parker 1984), and/or transport through low permeability soils or soil barriers (Acar and Haider, 1990; Shackelford and Redmond, 1995). The results of these simulations are illustrated in terms of dimensionless breakthrough curves (BTCs) for relative concentration \( (RC) \), relative fluxes \( (RF) \), and \( CMR \) in Figures 3.1, 3.2, and 3.3, respectively. The solutions of \( \alpha_m \) (Eq.2.30) and \( \beta_m \) (Eq.2.35) were limited to a maximum of
30,000 and 10,000 roots, respectively to achieve the accuracy necessary for \( P_L = 50 \). To allow for more efficient calculation, the limit of the maximum number of roots was decreased for lower \( P_L \) values. The first six roots of \( \alpha_n \) were validated against the first six roots published by Carslaw and Jaeger (1959) and shown in Table 3.1. The constant value \( C \) in Carslaw and Jaeger equation is equivalent to \( P_L / 2 \). No published data for the roots of \( \beta_n \) were found. However, comparison of simulation results based on models RC.4, RF.4 and CMR.4 to those reported in Shackelford (1995b) indicated that the values used herein were correct.

In Figure 3.1, for \( P_L = 1 \), models RC.1, RC.3, and RC.4 predict \( c_r(L,t)/c_o = 0.5 \) at \( T \leq 1 \), which is consistent with results reported by Biggar and Nielsen (1960) and Shackelford (1988) who also found that \( c_r(L,t)/c_o \) for a non-reactive solute was less than 0.5 at \( T \leq 1 \) due to diffusion dominated transport at low flow rates (i.e., low \( P_L \)). However, model RC.2 predicts \( c_r(L,t)/c_o = 0.5 \) at \( T > 1 \), which is inconsistent with the dominance of diffusion at low flow rates. In general, as the value of \( P_L \) increases, advection becomes increasingly more dominate (i.e., \( v \) increases relative to \( D_h \) for a given \( L \)), such that the differences among the four models decrease. When advection dominates (i.e., \( P_L \geq 50 \)), the differences among the models become imperceptible (e.g., Shackelford 1994b).

The differences among the simulation results shown in Figure 3.2 based on the four relative flux models decrease as advection becomes increasingly more dominant (i.e., as \( P_L \) increases). For \( P_L \) values of 5 and 20, models RF.1 and RF.3 tend to yield similar results, whereas models RF.2 and RF.4 tend to yield similar results. When advection dominates (i.e., \( P_L \geq 50 \)), the differences among the models become imperceptible.

Relative flux model RF.1 results in values of relative effluent concentration, \( c_e/c_o \), greater than unity (i.e., \( c_e/c_o > 1 \)) for \( P_L = 1 \) during the transient portion of the simulation. Although
values of $RF$ emanating from the column of soil can exceed unity under diffusion dominated conditions (e.g., see Shackelford, 1990), effluent concentrations exceeding the source concentration, $c_o$, are not possible. Thus, the concentration model RC.1 cannot be used for the purpose of defining flux-averaged effluent concentrations. This failure of RC.1 to transform is expected, since the flux-averaged concentrations become increasingly invalid as $v$ decreases and are undefined for the case of pure diffusion (i.e., $v = 0$) (van Genuchten and Parker, 1984; Shackelford, 1994).

The results of the simulations using the relative flux model RF.2 are the same in Figure 3.2 as the those based on relative concentration model RC.1 in Figure 3.1, i.e., for the same values of $P_L$, since these two models have exactly the same mathematical form (compare Eq. 2.26 and 2.17, respectively). The relative effluent concentration model based on RF.2 also correctly accounts for the dominance of diffusive transport at low flow rates (Shackelford, 1994).

The results of the simulations for the cumulative mass ratio ($CMR$) are shown in Figure 3.3. For each model and each value of $P_L$, an increase in solute mass during an initial transient stage of the simulations is followed by a steady-state increase in solute mass represented by a one-to-one slope of $CMR$ vs $T$ (e.g., Shackelford 1995a). The differences in the simulation results among the four CMR models are the same as those for the RF model simulation results shown in Figure 3.2, i.e., since the CMR models were derived from the respective RF models presented in Table 2.3. Also, CMR.1 tends to yield the same result as CMR.3, and CMR.2 tends to yield similar results to CMR.4.
3.3 Retardation Factor

In traditional column testing, the retardation factor, $R_d$, is typically assumed to be equal to the value of the pore volumes of flow, $T$, at which the relative effluent concentration, $c_e/c_o$, is equal to 0.5 (Freeze and Cherry, 1979 and Shackelford, 1993). This correlation between $R_d$ and $T$ is only valid under advective dominated transport conditions, and does not provide an accurate assessment of mass balance for finite soil columns at low flow rates (van Genuchten and Parker, 1984; Shackelford, 1994b). Based largely on van Genuchten and Parker (1984), Shackelford (1994b, 1995a) noted that the retardation factor was more accurately represented by the area above the effluent breakthrough curve after steady-state transport conditions were achieved, commonly referred to as the "relative holdup," which can be expressed analytically as follows:

$$R_d = \int_0^{T_{ss}} \left(1 - \frac{c_e}{c_o}\right) dT = \int_0^{T_{ss}} dT - \int_0^{T_{ss}} \frac{c_e}{c_o} dT = T_{ss} - \int_0^{T_{ss}} \frac{c_e}{c_o} dT$$  \hspace{1cm} (3.1)

where $T_{ss}$ is the pore volumes of flow required to achieve steady-state transport.

Comparison of Eq. 2.22 to Eq.3.1 indicates that the second integral in Eq. 3.1 represents the $CMR$, representing a direct correlation between $CMR$ and $R_d$. Shackelford (1995b) substituted the four $CMR$ models from Table 2.3 into Eq. 3.1 to obtain the retardation factor as a function of $T$, $CMR$, and $P_L$. The resulting analytical expressions for $R_d$ from the four models are tabulated in Table 3.2 as a function of either $T_o$ or $(T-CMR)_{ss}$. As illustrated in Figure 3.4, $T_o$ represents the extension of the trend in $T$ versus $CMR$ at steady-state transport to the $T$-axis (i.e., x-intercept at steady state), whereas $(T-CMR)_{ss}$ represents the extension of the trend in $T$ versus $T-CMR$ at steady-state transport to the $T-CMR$ axis (i.e., y intercept).
Values of $T$-CMR are plotted in Figure 3.5 as a function of $T$ for each of the four CMR models. The plots of $T$ versus $T$-CMR also illustrate that $R_d = 1$ for all four models as advective flow become more dominant ($P_L = 50$).

### 3.4 Effect of Retardation Factor

The value of the retardation factor is greater than unity ($R_d > 1$) for reactive solutes. As a result, the BTCs should shift to the right relative to the $T$ axis as $R_d$ increases. The $RC$, $RF$, and $CMR$ models were evaluated for $P_L$ value of 20 with $R_d$ values of 1, 2, and 3, the plots of these analyses are illustrated in Figure 3.6, 3.7, and 3.8, respectively. As indicated in all three figures, all the BTCs shift towards the right with each incremental increase in the value of $R_d$.

For the $RC$ models, the value of 0.5 is centered above the $T = R_d$ (see Figure 3.6) which is consistent with results found by Freeze and Cherry (1979) and Shackelford (1993) for advective dominated transport. As required, the values of $T_o$ resulting from extending the steady-state trends resulting from the CMR model simulations shown in Figure 3.8 are equal to the respective values of $R_d$ used in the simulations for CMR.2 and CMR.4. $T_o$ resulting from extending the steady-state of models CMR.1 and CMR.2 fall short of the $R_d$ values they were evaluated for.

The results in Figure 3.8 for a $P_L$ of 20 are replotted in Figure 3.9 in the form of $T$-CMR versus $T$ for values of $R_d$ of 1, 2, and 3. The analytical expressions for $R_d$ from the four models are tabulated in Table 3.2 as a function of $(T$-$CMR)_s$. Only models CMR.2 and CMR.4 have $(T$-$CMR)_s = R_d$ for steady-state transport for all flow rates, and are independent of $P_L$. Models CMR.1 and CMR.3 are slightly below the pore volume of flow equal to $R_d$. Models CMR.1 and CMR.3 are dependent on $P_L$ and the analytical expression do of $R_d$ derived from Eq.10 are not correct. Model CMR.4 requires the summation of over 500 roots for $P_L = 20$ and 10,000 roots for
$P_L = 50$. Therefore, due to the computational efficiency of CMR .2 relative to CMR.4, model CMR.2 is the recommended for evaluation of $R_d$. 
Table 3.1 The first six roots of $\alpha_m$ for $\alpha_m \cot \alpha_m + C = 0$ (Carslaw and Jaeger, 1959)

<table>
<thead>
<tr>
<th>C</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_3$</th>
<th>$\alpha_4$</th>
<th>$\alpha_5$</th>
<th>$\alpha_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>0</td>
<td>4.4934</td>
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Table 3.1 (continued). The first six roots of $\alpha_m$ for $\alpha_m \cot \alpha_m + C = 0$ (Carslaw and Jaeger, 1959)

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<th>$\alpha_3$</th>
<th>$\alpha_4$</th>
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Note: The roots are all real if $C > -1$. 
Table 3.2 Analytical expressions for retardation factor \((R_d)\) as a function of pore volumes of flow \((T)\), cumulative mass ratio (CMR), and column Péclet number \((P_L)\) (from Shackelford 1995b)

<table>
<thead>
<tr>
<th>CMR Model</th>
<th>(R_d) from a plot of (T) vs. CMR</th>
<th>(R_d) from a plot of (T) vs. (T-CMR)</th>
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<tr>
<td>CMR.4</td>
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</tr>
</tbody>
</table>

\(T_o = \) Pore volume intercept corresponding to steady-state transport; 
\((T-CMR)_{ss} = \) Value of \(T-CMR\) at steady-state transport.
Figure 3.1 Four analytical models for relative concentration at $x=L$ as a function of Péclet number ($P_L$) for a retardation factor of unity ($R_d = 1$).
Figure 3.2 Four analytical models for relative solute flux as a function of the column Péclet number ($P_L$) for a retardation factor of unity ($R_d = 1$).
Figure 3.3 Four analytical models for cumulative mass ratio as a function of the column Péclet number ($P_L$) for a retardation factor of unity ($R_d = 1$).
Figure 3.4 Schematic of cumulative mass data versus pore volumes of flow illustrating the evaluation of the retardation factor \( (R_d) \). (a) pore volume intercept \( (T_o) \) corresponding to steady-state transport (b) \( T-CMR \) for steady-state transport \( (T-CMR)_{ss} \) (from Shackelford 1995b)
Figure 3.5 Results of the four cumulative mass ratio models plotted in terms of pore volumes of flow minus cumulative mass ratio (T-CMR) versus pore volumes of flow as a function of the column Péclet number ($P_L$) for a retardation factor of unity ($R_d = 1$).
Figure 3.6 Breakthrough curves for relative solute resident concentration based on the four analytical models as a function of retardation factor \( (R_d) \) for a Péclet number \( (P_L) \) of 20.
Figure 3.7 Breakthrough curves for relative solute flux based on the four analytical models as a function of retardation factor ($R_d$) for a Péclet number ($P_L$) of 20.
Figure 3.8 Breakthrough curves for cumulative mass ratio based on the four analytical models as a function of retardation factor ($R_d$) for a Péclet number ($P_L$) of 20.
Figure 3.9 Results of the four cumulative mass ratio models plotted in terms of pore volumes of flow minus cumulative mass ratio versus pore volumes of flow as a function of retardation factor ($R_d$) for a Péclet number ($P_L$) of 20.
CHAPTER 4 – USER MANUAL

4.1 System Requirements

The program is primarily accessed through Excel and utilizes Visual Basic for Application (VBA) programming language to automate calculations and processes. Matlab was utilized as a computational tool. The following system requirements are required to run the program:

- Microsoft® Excel (Version 14.0.4763.1000, 2010, Microsoft Corporation, Redmond, WA)
- Matlab (Version 7.11.0.584, R2010b, MathWorks, Natick, MA) with Spreadsheet Link EX installed.

Ensure that the following items in Microsoft® Excel are installed or activated prior to opening the program:

- Excel Add-in “Active Analysis ToolPak”
- Excel Add-in “Active Analysis ToolPak – VBA”
- Excel Add-in “Spreadsheet Link EX 3.1.2 for use with MATLAB and Excel 2007/2010”
- Excel VBA Reference “SpreadsheetLink2007_2010”

See Appendix A on steps to configure Excel for the Spreadsheet Link EX Add-In.

4.2 Opening the Program

Once the system requirements are fulfilled, open the Excel File titled "Analytical models for CMR testing in Excel-Matlab" and enable the macro (see Fig. 4.1). The first sheet is the main...
user sheet (see Fig. 4.2), where the Data Input and Graphing forms of the program can be opened.

### 4.3 Data Input Form

The first page of the Data Input Form (Figure 4.3) allows the user to select the models to analyze. To view the analytical equations, click on the "View Equations" button that will display the equations in a separate box (see Fig. 4.4). The second page of the Data Input Form allows the user to input the data parameters required for the simulations. The Data Input Form allows for a maximum of four simulations for each model. Operating the program for all 12 possible outcomes (i.e., Models 1, 2, 3, and 4 with outputs providing \( RC, RF, \) and \( CMR \)) and all four simulations will provide 48 sets of results. These calculations may take a few minutes to complete, depending on the value of the Péclet Number (\( P_L \)). A separate box will be visible while the program runs to keep the user informed of the progress.

There are five user defined parameters required to perform a simulation: (1) the retardation factor, \( R_d \); (2) the Péclet Number, \( P_L \); (4) the Initial Pore Volume, \( T_0 \); (4) the Incremental Pore Volume, \( T_{\text{inc}} \); and (5) the Maximum Pore Volume, \( T_{\text{max}} \). All models are undefined for pore volume \( T \) equal to zero \( (T = 0) \). The initial value of the pore volume \( T_0 \) is dependent on the value of \( P_L \), the initial pore volumes for each range of \( P_L \) values are listed in Table 4.1. The smaller the value of \( T_{\text{inc}} \), the more refined the analysis with respect to \( T \).

For Model 3 (\( RC.3, RF.3, CMR.3 \)) and Model 4 (\( RC.4, RF.4, CMR.4 \)), analyses require the solutions of equations with multiple roots and large series summations. Excel is unable to handle these types of calculations efficiently. Therefore, Matlab was employed to handle the calculations of Models 3 and 4. Each model requires the solution of either \( \alpha_m \) or \( \beta_m \) roots, the
number of maximum roots is dependent on the value $P_L$ and summarized in Tables 4.2 and 4.3 respectively. When advection dominates relative to dispersion/diffusion, the number of roots increases to reach the solution of the analytical models. As a result, the program is limited to $P_L = 50$ for Models 3 and 4. The user will receive an error message if the $P_L$ is greater than 50 prior to running calculations. The program will take longer to calculate for Models 3 and 4 if the $P_L$ value for $RC$, $RF$, and $CMR$ are not the same, since each model will require a separate solution of roots.

The first time the user opens the "Input Form," all model selection boxes and parameter inputs will be blank. Additional buttons have been included to provide for quicker input and changes to parameter data. The user can input default values by selecting the "Default Values" button (see Figure 4.6). A "Clear All" and "Select All" button have been provided on both pages to allow quicker selection of the model and run boxes.

Once the chosen model calculations are performed by the program, the "Input Form" and "Progress" windows will close. The user then can view the graphs by selecting on any of the four chart sheets (i.e. "Chart RC", "Chart RF", "Chart CMR", or "Chart T-CMR"). When the user opens the "Input Form" from the start page after the initial use, the form will display the previous input data. The input boxes for the four input variables have been programmed to be hidden from the user if none of the four models are selected for $RC$, $RF$, or $CMR$.

### 4.4 Graphing User Form

There are four graphs for the user to view the plotted results for of $RC$, $RF$, $CMR$, and $T$-$CMR$. Each graph can plot all 16 results (i.e., $RC$, $RF$, $CMR$, and $T$-$CMR$ values of for all four
runs) and can be difficult to compare when viewing all at once. The "Graphing Form" allows the user to toggle on and off results plotted on the RC, RF, CMR, or T-CMR plots (see Fig. 4.7).

4.5 Plotting Measured Data

The user can compare measured data (i.e., measured values of RC, RF, or CMR) against the four analytical models for RC, RF, and CMR by pasting the data into the second page of the workbook titled "Measured Data" (see Fig. 4.8). This option is activated via an on-and-off toggle switch in the "Graphing Form", which is activated by selecting the "Graphing Form" button on either the "Measured Data" or "Start" page. The "Measured Data" page will calculate T-CMR values.

4.6 Exporting Data

To export the output results into a new workbook, the user must select the "Export Data" button on the "Start" page. The user can view the output results on the "Export Data" page. An example of the "Export Data" page is shown in Fig. 4.9.

4.7 Hidden Sheets

Some work sheets in Excel used for calculation purposes have been hidden during normal operations, and to prevent the user from inadvertently changing the program calculation. These sheets can be unhidden by selecting the "Show All Sheets" button on the Start page, and can subsequently be hidden with the "Hide Sheets" button.
Table 4.1 Suggested input values for the Initial Pore Volume, $T_o$

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<th>Initial Pore Volume, $T_o$</th>
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</tr>
<tr>
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</tr>
<tr>
<td>$40 \leq P_L \leq 50$</td>
<td>$1.0 \times 10^{-3}$</td>
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</table>

Table 4.2 Number of maximum alpha roots ($\alpha_m$)

<table>
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<th>$P_L$</th>
<th>Maximum Alpha Roots ($\alpha_m$)</th>
</tr>
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<td>$40 \leq P_L \leq 50$</td>
<td>30,000</td>
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Table 4.3 Number of maximum alpha roots ($\beta_m$)

<table>
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<th>Maximum Beta Roots ($\beta_m$)</th>
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Figure 4.1 Enable Security for Macro.
Figure 4.2 Start Page.
Figure 4.3 Data Input Form – Select Models to Analyze.
**Figure 4.4 Model Equations – Model 1.**

<table>
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<tr>
<th>Upper (Influent) Boundary Condition</th>
<th>Lower (Effluent) Boundary Condition</th>
<th>Model Designation</th>
<th>Model</th>
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<td>$c_z/0,t = c_0$</td>
<td>$\frac{\partial c_z}{\partial x} (c_0,t) = 0$</td>
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<td>$\frac{c_z}{c_0} (L,t) = 0.5 \left{ \text{erfc}\left( \frac{1-T_z}{2\sqrt{T_z/P_L}} \right) + \exp\left( P_L \text{erfc}\left( \frac{1+T_z}{2\sqrt{T_z/P_L}} \right) \right) \right}$</td>
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<td></td>
<td>RF.1</td>
<td>$RF = 0.5 \left{ \text{erfc}\left( \frac{1-T_z}{2\sqrt{T_z/P_L}} \right) + \frac{2}{\sqrt{\pi T_z P_L}} \exp\left( -\frac{(1-T_z)^2}{2T_z/P_L} \right) \right}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CMR.1</td>
<td>$CMR = \frac{0.5R_d}{P_L} \left( P_L T_z - P_2 + 1 \right) \text{erfc}\left( \frac{1-T_z}{2\sqrt{T_z/P_L}} \right) + \exp\left( P_L \text{erfc}\left( -\frac{1+T_z}{2\sqrt{T_z/P_L}} \right) \right)$ $+ \frac{2}{\pi} \sqrt{T_z P_L} \exp\left( -\frac{(1-T_z)^2}{4T_z/P_L} \right)$</td>
</tr>
</tbody>
</table>

(1) $T = \frac{v_z}{L}$; $T_z = \frac{T}{R_d}$; $P_2 = \frac{v_z L}{D_h}$
Figure 4.5 Data Input Form – Input Parameters.
Figure 4.6 Data Input Form – Default Values.
Figure 4.7 Graphing Form.
Figure 4.8 Measured Data

<table>
<thead>
<tr>
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<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
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<td>MEASURED DATA</td>
<td>(k/f_a)</td>
<td>RR</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td></td>
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</table>
Figure 4.9 Export Data
CHAPTER 5 SUMMARY AND CONCLUSIONS

The four analytical models for relative concentration ($RC$), relative flux ($RF$), and cumulative mass ratio ($CMR$) presented and evaluated by Shackelford (1995b) were programmed in Excel and Matlab. Excel allowed the development of user forms to perform the simulations.

The results of simulations performed using the programmed models for the case of a non-reactive, non-sorbing chemical species corresponding to a retardation factor, $R_d$, of unity ($R_d = 1$) and values for the column Péclet number, $P_L$, of 1, 5, 20, were compared with those previously published by Shackelford (1995b) to ensure accuracy with respect to the programmed models. The comparison indicated that all of the programmed models were accurate over the range of $P_L$ values used in the simulations. These simulations including determining values of $RC$, $RF$, $CMR$ and the difference between the pore volumes of flow, $T$, and $CMR$, or $T-\text{CMR}$, as a function of $T$ for values of the retardation factor, $R_d$, of 1, 2, and 3, and varying column Péclet numbers, $P_L$, of 1, 5, 20, and 50. The simulation results for $RC$, $RF$, $CMR$, and $T-\text{CMR}$ for $R_d = 1$ and $P_L$ of 1, 5, and 20 accurately reproduced the results previously reported by Shackelford (1995b).

Simulations also were conducted with $R_d = 1$ for $P_L = 50$ to provide a comparison of results for a higher $P_L$ value where advective solute transport should be dominant relative to diffusive solute transport. This comparison indicated that the differences among the four models become increasingly less perceptible with an increase in $P_L$ due to the increasing dominance of advection relative to diffusion, such that the differences among the four models are virtually imperceptible at $P_L = 50$. Of the four models simulated by the program only CMR.2 and CMR.4 correctly show the steady-state intercept to the $x$ or $T$-axis equal to the $R_d$ the program evaluated for at any flow rate and any $R_d$ value.
Simulations also were performed for $P_L = 20$ and varying $R_d$ of 1, 2, and 3 to illustrate the effect of reactive solutes ($R_d > 1$) to the models. As expected, the program produced results with the model breakthrough curves shifted to the right on the $x$- or $T$-axis with each incremental increase in the value of $R_d$.

The programmed solution has some limitations. First, the maximum $P_L$ value has been limited to $P_L = 50$ due to the computational efficiency of analyzing the roots of $\alpha_m$ and $\beta_m$ for Models 3 and 4. The solutions of $\alpha_m$ and $\beta_m$ were limited to a maximum of 30,000 and 10,000 roots, respectively to achieve the accuracy necessary for $P_L = 50$, and advective dominated solute transport can be adequately modeled by the program for $P_L = 50$. Also, since all models are undefined for a value of $T$ equal to zero ($T = 0$), the program can automatically assign a recommended initial pore volume, $T_o$, value that is dependent on $P_L$ or the user can input their own $T_o$.

A user manual was developed to assist future users with the developed program. The program is accessed through Excel and will only use Matlab to solve Models 3 and 4. The program allows for the analyses of all 12 possible outcomes (i.e., Models 1, 2, 3, and 4 with outputs providing $RC$, $RF$, and $CMR$) and all four simulations will provide 48 sets of results. Graphs have been included in the program to plot the results for $RC$, $RF$, $CMR$, and $T$-$CMR$. A "Graphing Form" can be used to toggle on and off plots for ease of comparison. The program also allows the user to export the program output data into a separate workbook, this allows the user to plot results in a separate graphing software if they so choose. This program can be used as a tool for class or laboratory setting to illustrate the effects of transport parameters on contaminant transport through porous media.
REFERENCES


Matlab (R2010b) Version 7.11.0.584. MathWorks, Natick, MA.


APPENDIX A CONFIGURING EXCEL

A.1 Enable Excel Add-Ins in Microsoft® Excel 2010

To enable the Excel Add-Ins, start a Microsoft® Excel session and follow these steps:

1. Select File from the main menu.
2. Click Options. The Excel Options dialog box appears.
3. Click Add-Ins.
4. From the Manage selection list, choose Excel Add-Ins.
5. Click Go. The Add-Ins dialog box appears.
6. Select the check-boxes for "Analysis ToolPak" and "Analysis ToolPak – VBA" (see Fig. A.1)

The following are steps for the Spreadsheet Link EX Add-In:

7. Click Browse.
8. Select matlabroot\toolbox\exlink\exclink2007.xlam.
9. Click Open. In the Add-Ins dialog box, the Spreadsheet Link EX for use with MATLAB check box is now selected.
10. Click OK to close the Add-Ins dialog box.
11. Click OK to close the Excel Options dialog box.

The Spreadsheet Link EX Add-In loads now and with each subsequent Excel session.

The MATLAB group appears on the top right of the Home tab in your Excel worksheet:

A.2 Adding Spreadsheet Link EX to Visual Basic Editor

Follow these steps to enable the Spreadsheet Link EX software as a Reference in the Microsoft® Visual Basic® Editor 2010:
1. Open **Developer** tab, or press Alt+F11 (for instructions how to display the Developer tab, see Excel Help).

2. In the Visual Basic toolbar, click **Tools > References**.

3. In the "References — VBA Project" dialog box, select the **SpreadsheetLinkEX** check box (see Fig. A.2).

4. Click **OK**.

5. If the check box is unavailable follow steps 7 to 9 in section A.1.

![Figure A.1 Enable Excel Add-Ins](image)
Figure A.2 Reference Spreadsheet Link in VBA