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# Mathematical Description of Adsorption and Transport of Reactive Solutes in Soil: A Review of Selected Literature

C. C. Travis

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# MATHEMATICAL DESCRIPTION OF ADSORPTION AND TRANSPORT OF REACTIVE SOLUTES IN SOIL: A REVIEW OF SELECTED LITERATURE

C. C. Travis

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# MATHEMATICAL DESCRIPTION OF ADSORPTION AND TRANSPORT OF REACTIVE SOLUTES IN SOIL: A REVIEW OF SELECTED LITERATURE

C. C. Travis

## ABSTRACT

This report reviews selected literature related to the mathematical description of the transport of reactive solutes through soil. The primary areas of the literature reviewed are (1) mathematical models in current use for description of the adsorption-desorption interaction between the soil solution and the soil matrix and (2) analytic solutions of the differential equations describing the convective-dispersive transport of reactive solutes through soil.

# 1. INTRODUCTION

This study is a survey of selected aspects of the mathematical theory of the transport of reactive solutes through soil. It was undertaken as a first step toward improving and refining existing methodologies for assessing the impact of alternative energy-related technologies on man. The movement of reactive solutes through porous media is a fundamental process in the assessment of both nuclear and nonnuclear technologies. Even though there presently exist several reasonably good methodologies for predicting radionuclide movement in soil, there is a continuing need to upgrade these methodologies as the demand for accuracy and realism increases. It is expected that the state-of-the-art review provided by this document will assist in this process.

The study of the movement of reactive solutes through an absorbing medium has a long and varied history. Scientists from diverse areas of science and engineering have contributed to its development. In the area of chemical engineering, for example, the theory of solute transport has been used successfully to develop chromatography into a powerful tool for chemical separation and analysis. In agriculture, the movement of chemicals through the soil is of major importance in the study of soil fertility, as well as in pest control, irrigation, salinity control, and drainage. Considerable attention has also been given to solute transport in such disciplines as groundwater hydrology, soil physics, sanitary engineering, petroleum engineering, nuclear waste management, and environmental monitoring.

The movement of reactive solutes in soil is controlled by three processes: convection by moving water, hydrodynamic dispersion, and adsorption or exchange of the solutes by the soil matrix. The mathematical simulation of the transport of a reactive solute through soil therefore requires the simultaneous solution of the differential equation describing convective-dispersive transport and the equation describing the interaction between the solute and the soil matrix. This

report reviews these differential equations together with their mathematical solution.

The review is organized as follows. Section 2 contains definitions of selected soil and groundwater terms that arise in the mathematical simulation of the transport and adsorption of reactive solutes in soil. In Sect. 3, a brief review of the differential equations describing convective-dispersive solute transport in porous media is presented. Sections 4 and 5 are devoted to a review of mathematical models in current use for description of the adsorption-desorption process in soil. Section 6 contains a review of selected literature related to analytic solutions of the differential equations describing convective-dispersive transport of reactive solutes in one dimension.

# 2. SOIL PROPERTIES

The soil is an exceedingly complex system composed of three phases: the solid phase consisting of soil particles, the liquid phase consisting of soil water together with dissolved substances, and the gaseous phase consisting of soil air. Each of these three phases has organic and inorganic constituents and possesses both inert and active compounds. The biological and heterogeneous character of soil strongly influences its physical and chemical properties. With regard to solute transport, the interaction of the diverse components in the soil has a direct effect on such phenomena as dispersion, convection, adhesion, adsorption, and ion exchange.

Reflecting this complexity, the problems of understanding and modeling the soil-water complex are numerous. In general, however, no unique physical or mathematical concepts beyond those common to the analysis of most other physical and biochemical systems are needed to simulate the transport of reactive solutes through the soil. These concepts include velocity and acceleration, potential and kinetic energy, force fields, and the conservation of energy, momentum, and mass. In this section, definitions of soil and soil-water characteristics are presented that are of use in the mathematical simulation of the transport and adsorption of reactive solutes in soil.

## 2.1 Bulk Density

The dry bulk density is the ratio of the mass of a dried soil to the total volume of the soil. The wet bulk density is the ratio of the mass of a moist soil to the total volume of the soil.

## 2.2 Porosity

The porosity is an index of the relative pore volume in the soil and is expressed quantitatively as the ratio of the volume of the soil interstices or voids to the total volume of the soil. Its value

generally is in the range 0.3 - 0.6 (30 - 60%). The effective porosity refers to the amount of interconnected pore space that is actually available for fluid transmission. It is expressed as the percentage of the total soil volume occupied by the interconnecting interstices.

## 2.3 Pore Velocity

The actual flow velocity of water in the soil is not uniform. The variability of velocity results from the facts that flow velocity near the center of a pore's cross section exceeds that near the edge and that the velocity in wide pores exceeds that in narrow pores. The average velocity of water through the pores is termed the pore velocity.

## 2.4 Darcy Flow Velocity

The Darcy flow velocity or Darcy flux is the volume of water passing through a unit cross-sectional area of soil per unit time. Darcy flow velocity and pore velocity are related by the fact that Darcy flow velocity equals the pore velocity multiplied by the effective porosity.

## 2.5 Volumetric Water Content

The volumetric water content or soil water content is the ratio of the volume of the soil solution to the total volume of the soil. In sandy soils its value at saturation is about 40-50%, in medium-textured soils it is approximately 50%, and in clay it can be on the order of 60%. When the soil is saturated with the soil solution, the volumetric water content is numerically equal to the effective porosity.

## 2.6 Soil-Water Potential

The soil-water potential is defined as the amount of work that must be done per unit quantity of pure water in order to transport an

infinitesimal quantity of water reversibly and isothermally from a pool of pure water at a specified elevation and atmospheric pressure to the soil water at the point under consideration. Stated simply, soil water potential is the energy that soil water possesses because of its relative position in the soil matrix. Differences in the potential energy of soil water within the soil matrix cause soil water to flow in the direction of decreasing potential energy. It is convenient to divide the total soil-water potential into four component potentials: (1) the gravitational potential, which is the energy of soil water resulting from its position in the gravitational field with respect to an arbitrary reference elevation; (2) the matric potential, which is the energy of soil water resulting from capillary and adsorption forces that tend to hold the soil water in the soil matrix; (3) the osmotic potential, which is a measure of the forces of attraction between dissolved ions and water molecules; and (4) the pneumatic potential, which is the energy of soil water resulting from unequal pressures in the gaseous phase.

## 2.7 Hydraulic Head

Soil water potential is expressible in several equivalent ways. Two of these are energy per unit mass and energy per unit volume. Since water is practically incompressible, the expression of potential as energy per unit mass is directly proportional to its expression as energy per unit volume. The dimensions of potential expressed as energy per unit volume are those of pressure.

The third, and often most convenient, method for expressing potential is in terms of hydraulic head, which is the height of a liquid column corresponding to a given pressure. Thus <u>hydraulic head</u> is the number of centimeters of a liquid, usually water, necessary to generate a pressure equal to that obtained when the potential is expressed in units of energy per unit volume.

## 2.8 Soil Moisture Retention Curve

The soil moisture retention curve gives the functional relationship between soil water content and suction. This curve is strongly dependent on the nature of the particular soil under consideration. Two typical soil moisture retention curves are shown in Fig. 1.

These curves show that if only a slight external suction is applied to the soil matrix, no outflow of soil water will occur. As suction is increased and exceeds a critical value, the largest pores begin to empty. Very soon most of the large pores will be empty, and outflow of soil water will begin in progressively smaller pores, until, at high suction values, only the very narrow pores will retain water. In a sandy soil, where most of the pores are relatively large, the water content decreases rapidly as suction increases. In a clayey soil, where the pore-size distribution is more uniform, there is a more gradual decrease in water content. Thus the amount of water remaining in the soil matrix at a given level of suction is strongly dependent on the size and distribution of the soil pores.

There are two different ways to obtain the relationship between suction and soil wetness. One is to measure water content vs suction while increasing suction to gradually dry a saturated soil. The other is to wet an intially dry soil while decreasing suction. The two methods do not yield the same results. Figure 2 shows typical results. The interested reader is referred to Miller and Miller (1955, 1956), Mualem (1973, 1974), and Parlange (1976) for a further discussion of this subject.

## 2.9 Breakthrough Curve

As a pulse of solute moves through a finite soil column, dispersion causes the solute to spread. Measurements as a function of time at the bottom of the soil column reveal that the solute concentration will gradually increase from zero to some maximum value in the form of an S-shaped curve. This curve is called a breakthrough curve.

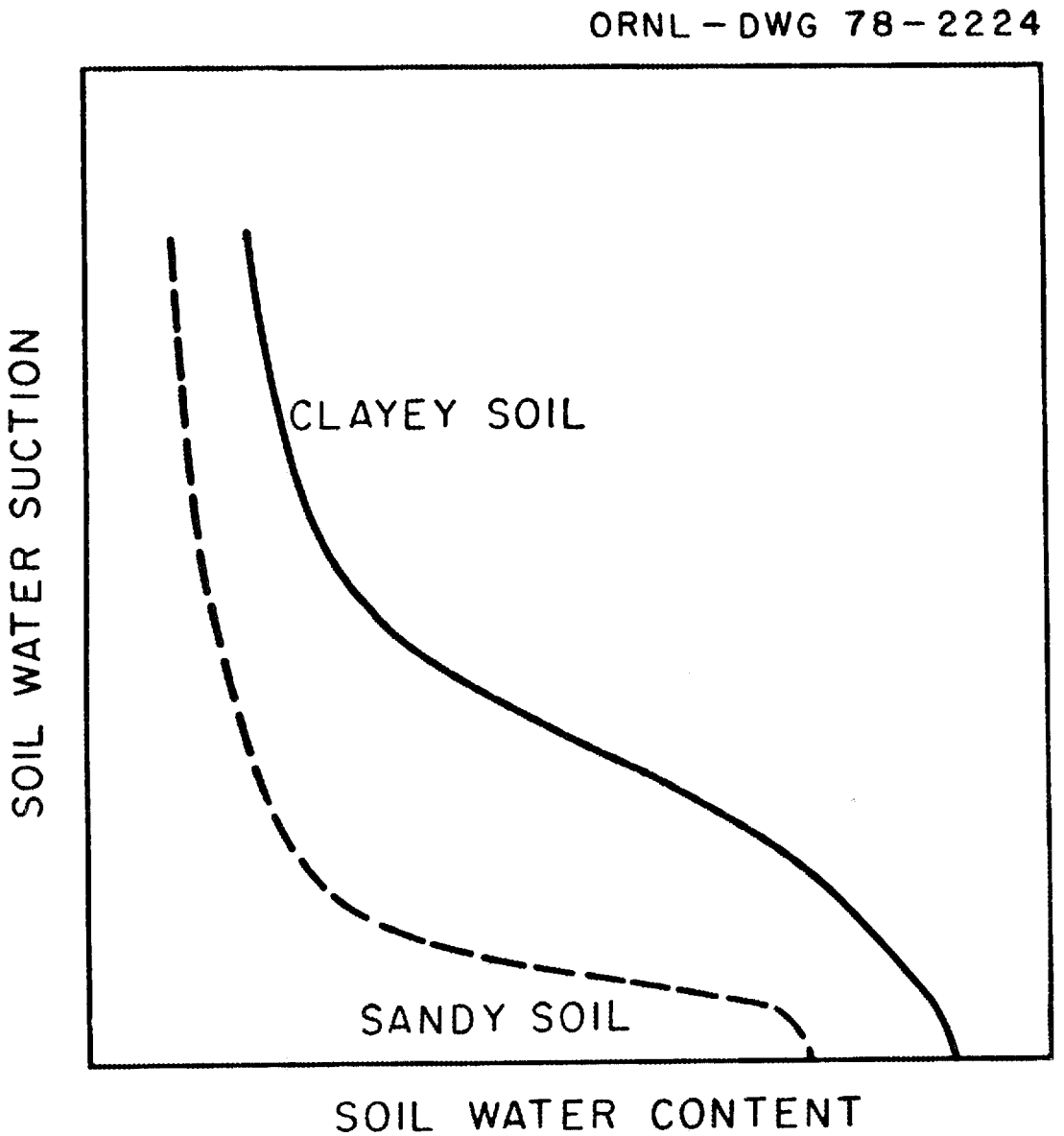


Fig. 1. Soil moisture retention curves depicting the functional relationship between soil water content and suction for two different types of soil

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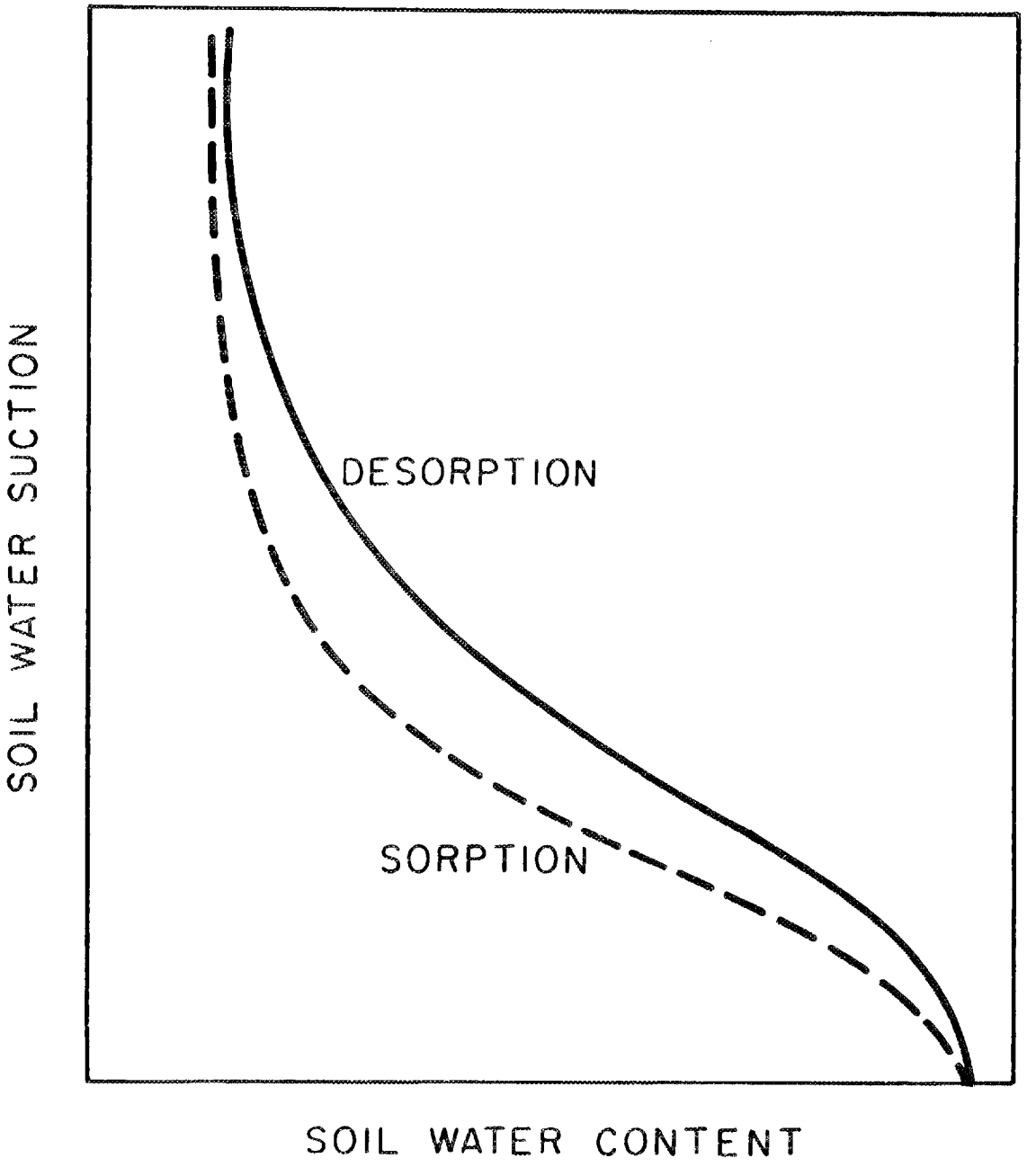


Fig. 2. Soil moisture retention curves obtained by sorption and desorption

## 3. CONVECTIVE-DISPERSIVE SOLUTE TRANSPORT

The theory of convective-dispersive solute transport in porous media has been discussed for many years, and its mathematical formulation is well understood. The mathematical derivation of this theory will not be discussed in detail, and the interested reader is referred to Bear (1972) and Crank (1956) for a development of the theory. This study will, however, present the relevant equations and briefly discuss the physical significance of their terms.

The differential equation governing convective-dispersive reactive solute transport in anisotropic media may be written as

$$\theta \frac{\partial C}{\partial t} = \theta \frac{\partial}{\partial x}\left(D_x \frac{\partial C}{\partial x}\right) + \theta \frac{\partial}{\partial y}\left(D_y \frac{\partial C}{\partial y}\right) + \theta \frac{\partial}{\partial z}\left(D_z \frac{\partial C}{\partial z}\right) - \frac{\partial}{\partial x}(q_x C) - \frac{\partial}{\partial y}(q_y C) - \frac{\partial}{\partial x}(q_z C) - \rho \frac{\partial S}{\partial t} - Q , \qquad (1)$$

where

$C$ = concentration of solute in soil solution ($\mu g/cm^3$),
$S$ = amount of solute adsorbed on soil matrix ($\mu g/g$),
$\rho$ = soil bulk density ($g/cm^3$),
$\theta$ = volumetric soil water content ($cm^3/cm^3$),
$D_x$ = x component of solute dispersion coefficient ($cm^2/hr$),
$D_y$ = y component of solute dispersion coefficient ($cm^2/hr$),
$D_z$ = z component of solute dispersion coefficient ($cm^2/hr$),
$q_x$ = x component of Darcy soil water flow velocity (cm/hr),
$q_y$ = y component of Darcy soil water flow velocity (cm/hr),
$q_z$ = z component of Darcy soil water flow velocity (cm/hr),
$Q$ = a sink (or source) for irreversible solute interaction [$\mu g/(cm^3 \cdot hr)$],
$z$ = distance from the soil surface (cm),
$t$ = time (hr),

The primary mechanism governing the transport of solutes in soils is the convection of the solute with water as water moves through the soil matrix. This process is represented in Eq. (1) by the terms

$$- \frac{\partial}{\partial x} (q_x C) - \frac{\partial}{\partial y} (q_y C) - \frac{\partial}{\partial z} (q_z C) \quad .$$

If this were the only mechanism governing the transport of solutes in soils, an amount of solute introduced into the soil solution would travel through the soil column in a body without any lengthening or spreading. In reality, the body of solute will grow in size because the soil solution does not move through the soil matrix in a uniform manner. The flow rate is slower near the walls of a soil pore than in the middle, the flow is faster in large pores than in small pores, and water flows in some pores at an angle to the mean direction of water flow. This tendency for molecules of a solute to become more diffuse with time is called hydrodynamic dispersion. Because this phenomenon can occur only when there is movement of the water through the soil, convection and hydrodynamic dispersion are two inseparable processes.

Another process causing the dispersion of the solute is molecular diffusion. This is caused by the random thermal motion of molecules in the soil solution and occurs whether there is water movement through the soil or not. However, since hydrodynamic dispersion and molecular diffusion are governed by differential equations of the same form, their effects can be added. The combination is referred to as apparent diffusion, and this process is represented in Eq. (1) by the terms

$$\frac{\partial}{\partial x}\left(D_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial C}{\partial z}\right) \quad .$$

In addition to convection, hydrodynamic dispersion, and molecular diffusion, the transport of a solute in the soil is affected by adsorption and exchange with the soil matrix. This reversible solute adsorption by the soil matrix is represented in Eq. (1) by the quality $\partial S/\partial t$.

We will assume that there is a functional relationship between S and C, which we may express as

$$S = f(C). \tag{2}$$

Such a relationship is termed an adsorption function or an adsorption isotherm. If we then replace $\partial S/\partial t$ in (1) by

$$\frac{\partial S}{\partial t} = f'(C)\,\frac{\partial C}{\partial t} \quad ,$$

we obtain

$$\begin{aligned}\theta\,\frac{\partial C}{\partial t} = {} & \theta\,\frac{\partial}{\partial x}\left[D_x(C)\,\frac{\partial C}{\partial x}\right] + \theta\,\frac{\partial}{\partial y}\left[D_y(C)\,\frac{\partial C}{\partial y}\right] \\ & + \theta\,\frac{\partial}{\partial z}\left[D_z(C)\,\frac{\partial C}{\partial z}\right] - \frac{\partial}{\partial x}\,[q_x(C)C] - \frac{\partial}{\partial y}\,[q_y(C)C] \\ & - \frac{\partial}{\partial z}\,[q_z(C)C] - Q(C)\ ,\end{aligned} \tag{3}$$

where

$$D_x(C) = D_x/\left(1 + \frac{\rho}{\theta}\,f'(C)\right)$$

$$q_x(C) = q_x/\left(1 + \frac{\rho}{\theta}\,f'(C)\right)$$

$$Q(C) = Q/\left(1 + \frac{\rho}{\theta}\,f'(C)\right)\ .$$

The factor $1 + (\rho/\theta)\,f'(c)$ has been called the retardation factor by Hashimoto et al. (1964). The physical significance of the retardation factor is that the ratio of the Darcy velocity to the solute migration velocity is given by this factor.

# 4. EQUILIBRIUM ADSORPTION MODELS

One problem in attempting to model solute transport in the soil is the development of an adsorption-desorption function that describes the relationship between the concentration of the solute in the soil solution and the amount of the solute adsorbed on the soil matrix. The adsorption-desorption process in the soil can be a kinetic one in which the relative amounts of the solute in the soil solution and in the soil matrix are changing with time, or it can be an equilibrium situation in which the equilibrium ratio between amounts of solute in the soil solution and in the soil matrix is attained rapidly and thereafter remains constant. This section will review the mathematical models that have been used in the literature to describe the adsorption-desorption process under equilibrium conditions.

## 4.1. Linear Adsorption Isotherm

The simplest and most widely used of the equilibrium adsorption isotherms is that given by a linear relationship. That is, it is assumed that the amount of the solute adsorbed by the soil matrix and the concentration C of the solute in the soil solution are related by the linear relationship

$$S = K_d C \ , \tag{4}$$

where $K_d$, the distribution coefficient, is a measure of the retention of the solute by the soil matrix. Experimentally, the distribution coefficient, $K_d$, can be determined from the ratio

$$K_d = \frac{[M]_{soil}}{[M]_{solution}} \ ,$$

where

$M_{[soil]}$ = amount of solute adsorbed by the soil matrix ($\mu g/g$),

$M_{[solution]}$ = concentration of solute in soil solution ($\mu g/cm^3$).

The assumptions implicit in the use of a linear isotherm are that the concentration of the solute in the soil solution is very low and that the equilibrium ratio between the soil solution and the soil matrix is attained rapidly.

The linear isotherm model (4), in conjunction with the convective-dispersive solute transport model (1), has been used frequently to describe the transport of radioactive material through porous media. Duguid and Reeves (1976) use equation (4) in a model of radioactive contaminant transport from a seepage pond, situated entirely above the water table, to a nearby stream. The results of the simulation, however, are not compared with empirical data.

Logan (1976) uses a linear adsorption isotherm, together with a two-dimensional convective-dispersive solute transport model, to perform an assessment of the quantitative effects on the environment resulting from the potential release of radionuclides during all phases of radioactive waste management operations.

Burkholder (1976) develops a transport model to predict radionuclide migration from geologic repositories should groundwater invade the disposal site. The dissolved nuclides may have complex physicochemical interactions with the soil as they migrate. These interactions cause the nuclides to move at lower velocities than the water and thereby reduce, as a result of radioactive decay during holdup, radioactivity releases to the biosphere. To simulate this adsorption of the nuclides by the soil matrix, Burkholder uses a linear equilibrium adsorption isotherm with a distribution coefficient $K_d$. The ratio of the water velocity to the nuclide migation velocity is then given by the retardation factor $K = 1 + \rho K_d/\theta$.

Van De Pol et al. (1977) employ a linear equilibrium adsorption isotherm in their study of the rate of movement of tritium in a soil

column under field conditions. When the predicted concentration of tritium in the soil was compared with experimental observations, the linear adsorption isotherm was found to adequately describe the adsorption of tritium by soil under the conditions of the experiment.

The linear isotherm model (4) has also been used to describe the adsorption of nonradioactive solutes by the soil matrix. Selim and Mansell (1976) use Eq. (4) to develop a model for solute transport in a finite soil column. The model has not been verified with experimental data, however.

Selim, Davidson, and Rao (1977) employ Eq. (4) in their study of solute transport through multilayered soils. Within each layer, the soil is assumed to be homogeneous and isotropic. The linear adsorption isotherm is used to describe solute adsorption within the individual soil layers. The predicted results were compared with experimental data on the movement of the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) through a two-layer soil column consisting of Norge loam and Eustic sand. The predicted and experimental data were found to be in close agreement. Elrick, Erh, and Krupp (1966) also used a linear adsorption isotherm to predict the movement of herbicides through the soil. Theoretical breakthrough curves based on the linear adsorption isotherm were found to describe the early breakthrough behavior of the herbicide Atrazine. The theoretical breakthrough curve predicted greater concentrations of the herbicide at later times than were measured experimentally, indicating a greater adsorption of the herbicide than predicted by the linear model. Lindstrom et al. (1967) also used the linear isotherm equation to develop a mathematical model of the movement of the herbicide 2,4-D in the soil.

Begovich and Jackson (1975) used a linear adsorption isotherm to simulate the six-year buildup of lead, cadmium, zinc, and copper around a lead smelter. It was found that the predicted levels of cadmium and zinc in the top two soil horizons were comparable with the experimentally determined values. Results obtained for lead and copper were not so satisfactory.

## 4.2 Freundlich Isotherm

The Freundlich isotherm is defined by the nonlinear relationship

$$S = KC^N \quad , \tag{5}$$

where K and N are constants. This isotherm is the oldest of the nonlinear adsorption isotherms and has been used widely to describe the adsorption of solutes by soils. It should be kept in mind, though, that the flexibility of the two constants allows for easy curve fitting but does not guarantee accuracy if the data are extrapolated beyond the experimental points. One limitation of the Freundlich isotherm is that, like the linear isotherm model, it does not imply a maximum quantity of adsorption.

Numerous examples exist in the literature where the Freundlich isotherm has been used to describe the adsorption of solutes by the soil matrix. To mention a few, Bornemisza and Llanos (1967) and Chao et al. (1962a, 1962b, 1962c, 1963) reported that sulfate adsorption by soils conformed to the Freundlich isotherm. Garcia-Miragaya et al. (1976), Levi-Minzi et al. (1976), and Street et al. (1977) found that the adsorption of cadmium by soils could be described using the Freundlich isotherm. Van Genuchten et al. (1974), Swanson and Dutt (1973), Lindstrom et al. (1967, 1970, 1971), Harris (1966, 1967), Geissbuhler et al. (1963), Oddson et al. (1970), Haque and Sexton (1968), Haque et al. (1968), Hornsby and Davidson (1973), Bailey and White (1970), Davidson and McDougal (1973), Hance (1967), Kay and Elrick (1967), Davidson and Chang (1972), and others proposed the use of the Freudlich isotherm to describe the movement of herbicides in the soil.

## 4.3 Langmuir Isotherm

The Langmuir adsorption isotherm was developed by Langmuir (1918) to describe the adsorption of gases by solids. Langmuir assumed that

the surface of a solid possesses a finite number of adsorption sites. If a gas molecule strikes an unoccupied site, it is adsorbed, whereas if it strikes an occupied site, it is reflected back into the gas phase. This model leads immediately to the concept of an upper limit of adsorption. The maximum amount of adsorption occurs when the surface of the solid is covered with a closely packed adsorbed layer of gas molecules.

The derivation of the Langmuir absorption isotherm presented by Langmuir for gases can be modified to apply to the adsorption of reactive solutes by soil. Each adsorption site in the soil matrix can be assumed to have an equal probability of adsorbing the solute from the soil solution. This assumption requires that the free energy of adsorption for the soil be constant. Under this assumption, the rate of adsorption will be proportional to the concentration of the solute in the soil solution and to the number of sites in the soil matrix that are as yet unoccupied. Thus the rate of adsorption of the solute by the soil matrix will be given by

$$K_1C(b - S) \quad , \tag{6}$$

where C is the concentration of the solute in the soil solution, S is the amount of the solute adsorbed by the soil matrix, b is the maximum amount of the solute that can be adsorbed by the soil matrix (μg/g), and $K_1$ is a constant. The rate of dissociation of the solute from the soil matrix will be proportional to the number of occupied sites in the soil matrix. Thus the rate of dissociation will be given by

$$K_2S \quad . \tag{7}$$

At equilibrium,

$$K_2S = K_1C(b - S) \quad . \tag{8}$$

Replacing $K_1/K_2$ by K and rearranging, we obtain the two standard forms of the Langmuir isotherm:

$$\frac{C}{S} = \frac{1}{Kb} + \frac{C}{b} \tag{9}$$

and

$$S = \frac{KbC}{1 + KC} \ . \tag{10}$$

In these two formulas, K is a measure of the strength of the bond holding the adsorbed solute on the soil surface, and, as was stated before, b is the maximum amount of the solute that can be adsorbed by the soil matrix (μg/g).

The monolayer adsorption theory of Langmuir breaks down when the free energy of adsorption is not constant. This is the case when the heat of adsorption of the solute by the soil matrix is not independent of the number of occupied adsorption sites in the soil matrix. However, several useful adsorption isotherms have been derived by assuming different functional relationships between the heat of adsorption of the solute by the soil matrix and the fraction of the adsorption sites in the soil matrix that is occupied by the solute. If the heat of adsorption is a linear function of the surface coverage, the adsorption isotherm takes the form used by Brunauer et al. (1942):

$$\log C = K_1 + K_2 S \ , \tag{11}$$

where $K_1$ and $K_2$ are constants. If the heat of adsorption is a logarithmic function of the surface coverage, the adsorption isotherm can be shown (Halsey and Taylor 1947) to be:

$$\log S = K + N \log C \ , \tag{12}$$

where K and N are constants. This is an equivalent form of the Freundlich isotherm, and it is thus seen that the Freundlich isotherm

may be obtained from Langmuir's theory of monolayer adsorption by assuming that the heat of adsorption is a logarithmic function of the surface coverage.

The Langmuir adsorption isotherm has been used extensively in the literature to describe the adsorption of solutes by the soil. For example, John (1972) and Levi-Minzi et al. (1976) found the Langmuir isotherm to adequately describe cadmium adsorption over a wide range of soil types. Colombera et al. (1971) found that the adsorption of aluminum from hydroxy-aluminum perchlorate solutions by clay minerals in the soil can be described by the Langmuir adsorption isotherm. Enfield and Bledsoe (1975) and Novak et al. (1975) used the Langmuir adsorption isotherm to model the movement of phosphorus in soils resulting from the renovation of wastewater by a land application treatment system. The Langmuir isotherm has also been used by Olsen and Watanabe (1957), Weir and Soper (1962), Pissarides et al. (1968), Obihara and Russell (1972), Wier (1972), Humphreys and Pritchett (1971), Rajan and Watkinson, (1976) and others to describe phosphorus adsorption by soil.

It can be seen from Eq. (9) that a plot of C/S against C should give a straight line of slope 1/b. Soil phosphate adsorption data obtained by Olsen and Watanabe (1957) and Larsen et al. (1965) indicate that in the case of phosphorus adsorption by soil, the plot of C/S against C is not a straight line. One possible explanation of these results is that the energy of adsorption of phosphorus by soil is not constant. Bache and Williams (1971) point out that for the data obtained by Olsen and Watanabe, the relationship between the energy of adsorption of phosphorus by soil and the surface coverage is almost linear. They therefore propose that an adsorption isotherm of the form (11) might be more appropriate for describing phosphate adsorption by soil. The experimental data obtained by Olsen and Watanabe are shown to be fitted satisfactorily by an adsorption isotherm of this form.

In a different attempt to account for the degree of curvature in the plot of C/S against C, Gunary (1970) did a least-squares fit of several different equations to the data for phosphate adsorption on 24

different soils obtained by Larsen et al. (1965). He concluded that the best fit was given by the equation

$$\frac{C}{S} = K_1 + K_2C + K_3\sqrt{C} \quad , \tag{13}$$

where $K_1$, $K_2$, and $K_3$ are constants. No theoretical foundation for Eq. (13) was given, but the author suggested that the inclusion of the square root term in the equation could be taken to imply that the soil will adsorb a little phosphate firmly, a slightly greater amount of phosphate less firmly, and so on until a limiting value is reached when all the components of the phosphate adsorption system are saturated.

### 4.4 Langmuir Two-Surface Isotherm

Experimental data on phosphorus adsorption by Shapiro and Fried (1959), Arambarri and Talibudeen (1959), de Haan (1965), Helyar et al. (1976), Munns and Fox (1976), and others suggest that two different types of surface adsorption sites are responsible for the adsorption of phosphorus. One of these adsorption sites has a high bonding energy and reacts rapidly with phosphorus, while the other has a lower bonding energy and reacts more slowly with phosphorus. Langmuir (1918) proposed an equation for describing the simultaneous adsorption of a gas by more than one surface. The adaptation of Langmuir's equation to the adsorption of a solute by a soil with two adsorbing components is

$$S = \frac{K_1b_1C}{1 + K_1C} + \frac{K_2b_2C}{1 + K_2C} \quad , \tag{14}$$

where $b_1$ and $b_2$ are the maximum quantities of solute that can be adsorbed by the two components and $K_1$ and $K_2$ are constants related to the bonding energies of the components.

Holford et al. (1974) have used the Langmuir two-surface equation to model phosphate adsorption by soil. In their consideration of 41 soils from southern England and eastern Australia, they obtained an excellent fit of the experimental data with the Langmuir two-surface equation.

# 5. FIRST-ORDER KINETIC ADSORPTION MODELS

The use of the equilibrium adsorption models reviewed in the previous section is based on the assumption that the equilibrium between the reactive solute in the soil solution and the soil matrix is obtained rapidly. For some chemicals in the soil, such as phosphorus, this is generally not the case, and in such cases, it is more appropriate to use a kinetic model to describe the adsorption-desorption relationship. This section will review the more important first-order kinetic adsorption-desorption models.

## 5.1 Reversible Linear Model

The most frequently used first-order kinetic adsorption model is

$$\frac{dS}{dt} = k_1 \frac{\theta}{\rho} C - k_2 S \quad , \tag{15}$$

where S is the amount of the solute adsorbed by the soil matrix, C is the concentration of the solute in the soil solution, $\theta$ is the volumetric soil water content, $\rho$ is the soil bulk density, and $k_1$ and $k_2$ are constants. Equation (15) assumes that the rate of solute adsorption by the soil matrix is related to the difference between what can be adsorbed at some concentration and what has already been adsorbed. The equilibrium isotherm associated with Eq. (15) is a linear isotherm such as is given by Eq. (4).

Equation (15) has been used frequently to describe the adsorption kinetics of chemicals by the soil. For example, Davidson and McDougal (1973) and Hornsby and Davidson (1973) used Eq. (15) to describe the adsorption of herbicides by the soil. Lindstrom et al. (1967, 1970), Davidson and Chang (1972), and Oddson et al. (1970) used Eq. (15) to describe the movement of several different organic chemicals in the soil. Cho (1971) used Eq. (15) to describe the convective transport of various oxides of nitrogen in the soil.

One of the most frequent applications of Eq. (15) has been in the description of the adsorption kinetics of phosphorus in soils. Among those who have used this equation to describe the movement of phosphorus through the soil are Shah et al. (1975), Novak et al. (1975), Novak and Adriano (1975), Enfield (1974), Enfield and Bledsoe (1975), Enfield and Shew (1975), Enfield et al. (1976), Cho et al. (1970), and Griffin and Jurinak (1974).

## 5.2 Reversible Nonlinear Model

Another first-order kinetic equation that has been used to describe the adsorption-desorption relationship between a reactive solute and the soil matrix is the nonlinear kinetic equation

$$\frac{dS}{dt} = k_1 \frac{\theta}{\rho} C^n - k_2 S \quad . \tag{16}$$

The parameters $k_1$, and $k_2$ (Giddings 1965) are called, respectively, the forward and backward adsorption rate coefficients. When the value of n is unity, Eq. (16) reduces to the reversible linear first-order kinetic adsorption process described by Eq. (15). The equilibrium isotherm associated with Eq. (16) is the Freundlich adsorption isotherm, given by (5).

Enfield and Bledsoe (1975) have used Eq. (16) with a value of n less than unity to model the adsorption of herbicides by soil. Davidson and McDougal (1973) and Enfield, Harlin, and Bledsoe (1976) found that phosphorus movement in the soil could be described using Eq. (16) with a value of n less than unity.

Mansell et al. (1977) used Eq. (16) to predict the transport of phosphorus through sandy soils and found that it provided an adequate description of phosphorus transport in both water-saturated and water-unsaturated soils. This agreement between calculated and experimental data is not surprising, because in this experiment the backward and forward adsorption rate coefficients were extremely small

in relation to the average pore water velocities. The large average pore water velocities and the small adsorption rate coefficients caused the sorption of phosphorus from the soil to be small. This is consistent with general observations by Black (1968) that phosphorus applied to sandy and organic soils is more mobile than phosphorus applied to other soils.

Hornsby and Davidson (1973) used Eq. (16) to describe the transport of the organic pesticide fluometuron in soils. The distributions of the adsorbed and solution phases of the pesticide were well described at high flow rates. At low flow rates, where equilibrium adsorption exists, the kinetics of the adsorption process were not so important, and the process was described equally well using the linear adsorption isotherm (4).

Van Genuchten, Davidson, and Wierenga (1974) used Eq. (16) to study the movement of picloram (4-amino-3,5,6-trichloropicolinic acid) through a water-saturated Norge loam soil. The equilibrium adsorption and desorption isotherms were found to be described by different equations. When the observed and predicted concentrations of picloram in the soil were compared, it was found that Eq. (16) adequately described the adsorption kinetics at low pore water velocities (14.2 cm/day) provided the multivalued character of the adsorption-desorption process was included in the calculations. However, even at low pore water velocities, calculations using Eq. (16) did not fit the data as well as when a Freundlich adsorption-desorption relationship was assumed. At high pore water velocities (145 cm/day), Eq. (16) was found to be inadequate to predict picloram movement.

### 5.3 Kinetic Product Model

A model proposed by Enfield (1974) to describe the kinetics of phosphorus adsorption by soil is the equation

$$\frac{dS}{dt} = aC^bS^d \quad , \tag{17}$$

where a, b, and d are constants. This equation was empirically derived, and no theoretical foundation for its form is given. Moreover, like the Freundlich isotherm, it does not imply a maximum quantity of adsorption. These limitations aside, however, it has been used with some success by Enfield and others to describe phosphorus movement in soil.

Enfield found that the model provided an adequate description of phosphorus adsorption kinetics in five selected Oklahoma soils. He then compared the results of using Eq. (17) with those obtained using the reversible linear kinetic model (15). Even though the five soils had widely varying physical-chemical properties, in every case Eq. (17) gave a better fit to the experimental data than Eq. (15).

Enfield and Bledsoe (1975), using Eq. (17) to describe the transport in soil of phosphorus from a wastewater treatment system, reported that the predicted values fitted the experimental data reasonably well.

Enfield, Harlin, and Bledsoe (1976) compared Eqs. (15), (16), and (17), among others, in their ability to describe the kinetics of orthophosphate adsorption by 25 mineral soils under laboratory conditions. Equation (17) appeared to give the best overall results.

Enfield and Shew (1975) again compared the results of using Eq. (17) with those obtained using Eq. (15) for several different soils with soil textures ranging from sands through clays. Darcy flow rates ranged from 0.18 cm/hr (16 m/year) to 5.6 cm/hr (490 m/year). The majority of the studies were performed at the low end of the flow spectrum, since the model's primary objective was to describe the movement of phosphorus in wastewater treatment systems applying waste to land. Similar results were obtained in all soils studied. Of the two models tested, the one employing Eq. (17) appeared to give the best results.

## 5.4 Bilinear Adsorption Model

The kinetic version of the Langmuir adsorption isotherm (9) is given by the so-called bilinear adsorption model,

$$\frac{dS}{dt} = k_1C(b - S) - k_2S \quad , \tag{18}$$

where $k_1$ and $k_2$ are constants and b is the maximum quantity of solute that can be adsorbed by the soil matrix. The theoretical foundation for this equation is the same as that given for the Langmuir adsorption isotherm. We assume that the rate of adsorption of the solute by the soil matrix is proportional to the concentration of the solute in the soil solution and to the number of sites in the soil matrix that are as yet unoccupied. Thus the rate of adsorption of the solute by the soil matrix is given by

$$k_1C(b - S) \ . \tag{6}$$

The rate of dissociation of the solute from the soil matrix is assumed to be proportional to the number of occupied sites in the soil matrix. Thus the rate of dissociation will be given by

$$k_2S. \tag{7}$$

Taking the difference between the rate of adsorption and the rate of dissociation, one obtains Eq. (18). The equilibrium isotherm for this equation is, of course, the Langmuir adsorption isotherm (9).

Despite its strong theoretical foundation, Eq. (18) has not received widespread application in describing the adsorption of chemicals by soil. One reason for this lack of application is that there does not exist an analytic solution of the coupled system (9) and (18), and hence any use of this system requires a numerical approximation. However, Eq. (18) has been applied to the study of the adsorption of phosphorus on clay minerals by Gupta and Greenkorn (1973).

## 5.5 Elovich Model

An equation developed by Roginsky-Zeldovich (1934), but now generally known as the Elovich equation, has been applied by a few

researchers to describe the adsorption of solutes by the soil. The Elovich equation has the form

$$\frac{dq}{dt} = A_1 e^{-B_2 q} \quad , \tag{19}$$

where $A_1$ and $B_2$ are parameters and q is the fraction of the adsorption sites in the soil matrix occupied by the solute. This equation has been applied to describe the kinetics of the absorption of gases on solids by Allen and Scaife (1966) and Hayward and Trapnell (1964). A theoretical discussion of the equation can be found in Low (1960), McLintock (1967), and Atkinson et al. (1971).

An Elovich-type equation was used by Atkinson et al. (1971) and Kyle et al. (1975) to describe the kinetics of phosphate adsorption on the surface of gibbsite. The equation employed was

$$\frac{dq}{dt} = Ae^{-Bq} - Ae^{-B} \quad , \tag{20}$$

where A, B, and q are defined as in Eq. (19). This model was found satisfactorily to describe the adsorption of a phosphate solution by gibbsite.

An Elovich-type equation derived by Lindstrom et al. (1971) was used by Van Genuchten et al. (1974) to study to movement of a pesticide through a water-saturated Norge loam soil. The equation is

$$\frac{dS}{dt} = k_1 \frac{\theta C}{\rho} e^{-bS} - k_2 Se^{bS} \quad , \tag{21}$$

where $k_1$ and $k_2$ are the forward and backward kinetic rate coefficients, respectively, b is similar to the surface stress coefficient described by Fava and Eyring (1956), and S, C, $\theta$, and $\rho$ are as defined previously for Eq. (9). The equilibrium adsorption isotherm associated with Eq. (21) is given by

$$S = \frac{\theta k_1 C}{\rho k_2} \exp(-2bS) \quad . \tag{22}$$

## 5.6 Fava and Eyring Model

In their study of the adsorption and desorption of detergents on a fabric surface, Fava and Eyring (1956) employed the first-order kinetic equation

$$\frac{d\phi}{dt} = 2k_1\phi \sinh b\phi \quad , \tag{23}$$

where $k_1$ and b are constants and $\phi$ is defined as the distance from equilibrium divided by the initial distance from equilibrium. Thus $\phi$ is given by

$$\phi(t) = \frac{S(t) - S(\infty)}{S(0) - S(\infty)} \quad , \tag{24}$$

where S(o) is the initial amount adsorbed and $S(\infty)$ is the equilibrium amount adsorbed. The agreement obtained by Fava and Eyring with experimental data was quite good.

Hague and Sexton (1968), Lindstrom and Boersma (1970), and Leenheer and Ahlrichs (1971) have also used Eq. (23) to model the adsorption of pesticides by soil and organic matter. Lindstrom and Boersma (1970) compared results obtained using this equation with those obtained using the Freundlich adsorption isotherm and the reversible linear model.

## 5.7 Combined Equilibrium and Kinetic Model

Cameron and Klute (1977) have used a combination of the linear equilibrium isotherm (4) in the form

$$S = k_3 \frac{\theta}{\rho} C \tag{25}$$

together with the first-order linear kinetic model, Eq. (15),

$$\frac{\partial S}{\partial t} = k_1 \frac{\theta}{\rho} C - k_2 S \quad , \tag{26}$$

where $k_1$ and $k_2$ are the adsorption and desorption rate constants, to develop an adsorption-desorption relationship that describes the rate of solute transfer between the solute and the solid phases of the soil. The reasoning behind this approach is that a chemical in the soil may react at different rates with different components of the soil matrix. For example, a chemical may be adsorbed rapidly by the various mineral surfaces in the soil but slowly by the soil organic matter. Cameron and Klute consequently assumed that the adsorption of solutes by the soil matrix is controlled by two types of reactions: one that is rapid and consequently obtains an almost instantaneous equilibrium and one that is slower and is best described as a kinetic reaction. If we represent the concentration of the adsorbed solute in the soil matrix resulting from the kinetic reaction by $S_1$ and the adsorbed concentration in the soil matrix resulting from the equilibrium reaction by $S_2$, then the total adsorption S can be obtained as the sum of $S_1$ and $S_2$, and the total rate of adsorption is given by

$$\frac{\partial S}{\partial t} = \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \quad . \tag{27}$$

Since

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\theta}{\rho} C - k_2 S \tag{28}$$

and

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\theta}{\rho} \frac{\partial C}{\partial t} \quad , \tag{29}$$

Eq. (27) may be written

$$\frac{\partial S}{\partial t} = k_1 \frac{\theta}{\rho} C - k_2 S + k_3 \frac{\theta}{\rho} \frac{\partial C}{\partial t} \, , \tag{30}$$

where $k_1$, $k_2$, and $k_3$ are the adsorption rate, desorption rate, and equilibrium constants respectively.

After a sufficiently long period of time the reaction described in Eq. (30) will reach equilibrium, with the resultant adsorption isotherm being

$$S = \frac{\theta}{\rho}\left(\frac{k_1}{k_2} + k_3\right) C \quad . \tag{31}$$

Since Eq. (31) is a linear adsorption isotherm, it is easily seen that a laboratory determination of the adsorption isotherm could tend to mask the kinetic component.

Cameron and Klute applied their combination equilibrium-kinetic model to data obtained by Elrick et al. (1966) on the movement of the herbicide Atrazine in soil and to data on phosphorus ($KH_2PO_4$) movement obtained by Cho et al. (1970). The best agreement was obtained for the data on Atrazine movement in soil. Figure 3 shows the breakthrough curve obtained by Elrick et al. for Atrazine in Honeywood silt loam. The solid line is the theoretical breakthrough curve calculated under the assumption that the adsorption of Atrazine by the soil matrix can be described by the linear equilibrium adsorption isotherm (31) alone. As can be seen, the early breakthrough pattern is well described by the theoretical curve; however, the experimental values of $C/C_0$ do not approach a value of unity as quickly as predicted by the linear adsorption theory. Figure 4 shows the fit of the Cameron-Klute model to the data obtained by Elrick et al.

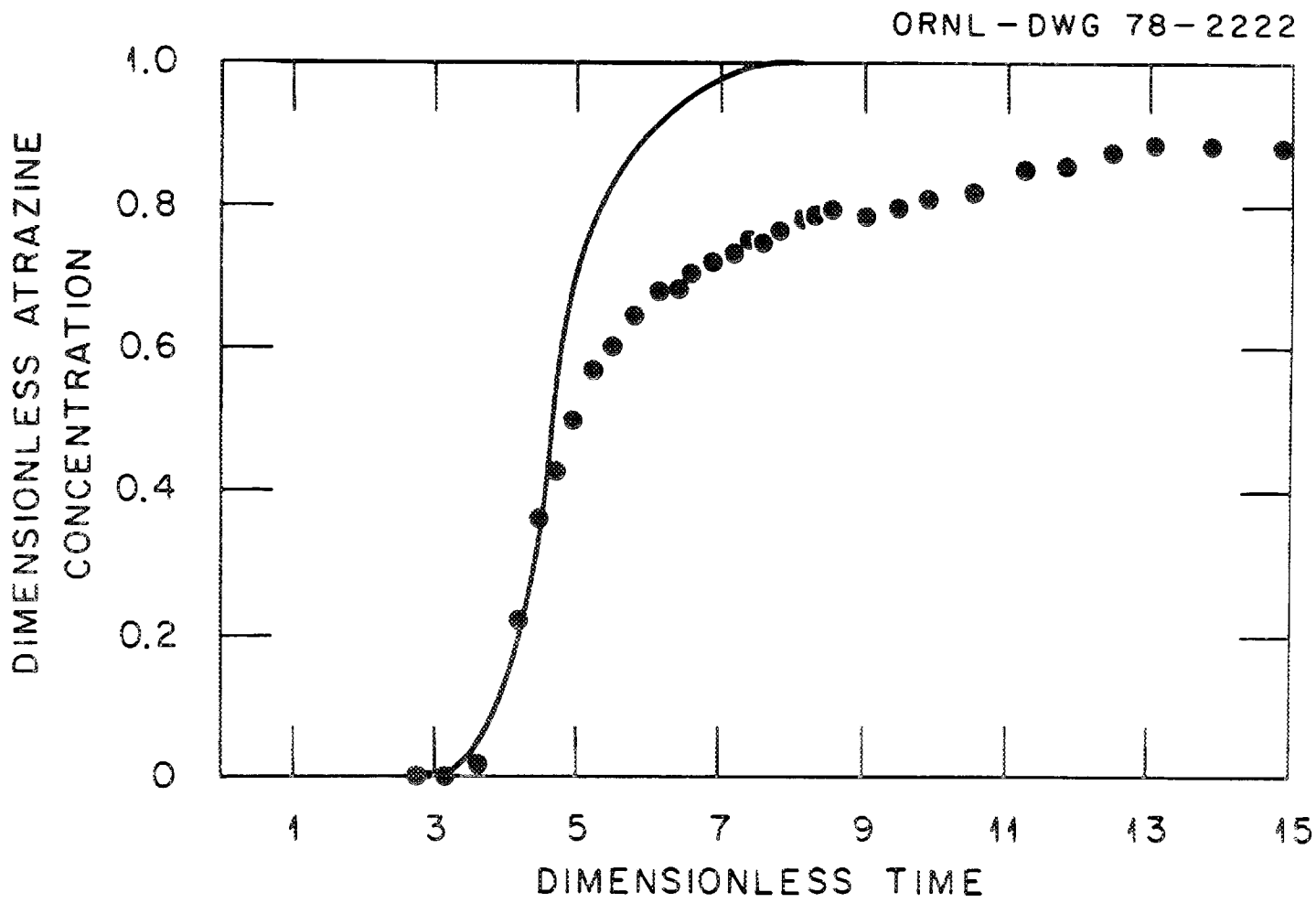


Fig. 3. Comparison of the theoretical breakthough curve calculated using a linear equilibrium adsorption isotherm with empirical data

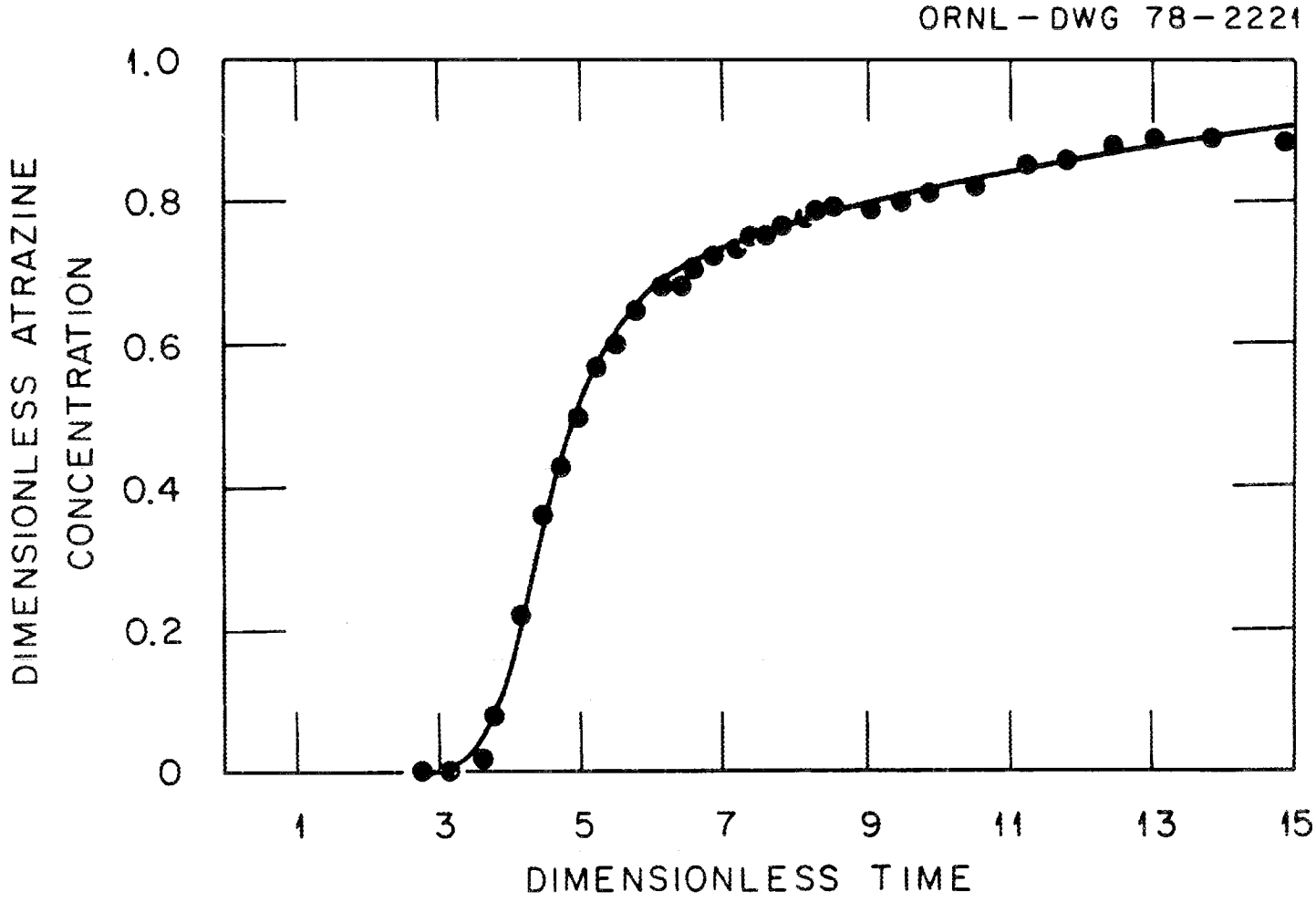


Fig. 4. Comparison of the theoretical breakthrough curve calculated using the Cameron-Klute model with empirical data

## 6. ANALYTIC SOLUTIONS OF TRANSPORT MODELS

As was discussed in Sect. 3, the differential equation governing convective-dispersive solute transport in anisotropic media is given by

$$\theta \frac{\partial C}{\partial t} = \theta \frac{\partial}{\partial x}\left(D_x \frac{\partial C}{\partial x}\right) + \theta \frac{\partial}{\partial y}\left(D_y \frac{\partial C}{\partial y}\right) + \theta \frac{\partial}{\partial z}\left(D_z \frac{\partial C}{\partial t}\right)$$
$$- \frac{\partial}{\partial x}(q_x C) - \frac{\partial}{\partial y}(q_y C) - \frac{\partial}{\partial z}(q_z C)$$
$$- \rho \frac{\partial S}{\partial t} - Q \ , \qquad (32)$$

where C is the concentration of the solute in the soil solution and S is the concentration in the soil matrix. Once the rate of solute adsorption by the soil matrix $\frac{\partial S}{\partial t}$ and the sink term Q have been specified, the simulation of the transport of a reactive solute by groundwater may be accomplished by the solution of this differential equation subject to various initial and boundary conditions.

A solution to Eq. (32) that can be written in closed form is called an analytic solution. Such solutions are difficult to obtain, and, in general, this equation must be solved by a numerical technique, such as the finite-element method or the finite-difference method. The difference equations that result from the application of these methods are generally solved with one of the following iterative methods: the line successive over-relaxation (LSOR) method described by Young (1954), the iterative alternating direction implicit procedure (ADI) as presented by Peaceman and Rackford (1955), or the strongly implicit procedure (SIP) introduced by Stone (1968). For a discussion and comparison of the various numerical methods used in solving Eq. (32), the interested reader is referred to Baetsle (1967), Shamir and Harleman (1967), Oster et al. (1970), Rubin and James (1973), Smith et al. (1973), Watts (1971, 1973), Aziz and Settari (1972), Pickens and Lennox (1976), Trescott and Larson (1977), and Mansell et al. (1977).

Most of the analytic solutions of Eq. (32) that have appeared in the literature are for the one-dimensional version of this equation. The one-dimensional version, under the assumption of constant coefficients and without the sink term, can be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} , \tag{33}$$

where V is the x component of the Darcy soil water flow velocity. This section reviews the various analytic solutions of this equation that have appeared in the literature.

## 6.1 Linear Isotherm

If a linear adsorption isotherm of the form $S = K_d C$ is assumed to exist between the soil matrix and the soil solution, then the one-dimensional equation (33) reduces to

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2} - V_0 \frac{\partial C}{\partial x} , \tag{34}$$

where $D_0 = D/(1 + \rho K_d/\theta)$ and $V_0 = V/(1 + \rho K_d/\theta)$. Solutions to Eq. (34), subject to various initial and boundary conditions, have appeared for both finite soil columns and semi-infinite soil columns. We will look at the semi-infinite case first.

### 6.1.1 Semi-infinite soil columns

The best-known solution of Eq. (34) was presented by Lapidus and Amundson (1952). Assuming initial conditions of the form

$$\begin{aligned} C(x, 0) &= Z_0(x), \quad x > 0 , \\ C(0, t) &= C_0(t), \quad t \geq 0 , \end{aligned} \tag{35}$$

the solution of (34) presented by Lapidus and Amundson is

$$C(x, t) = \exp\left(\frac{V_0 x}{2D_0} - \frac{V_0^2 t}{4D_0}\right)[f_1(x, t) + f_2(x, t)] , \tag{36}$$

where

$$f_1(x, t) = (4\pi D_0 t)^{-1/2} \times \int_0^\infty Z_0(s) \left[\exp\left(\frac{-V_0 s}{2D_0}\right)\right]\left\{\exp\left[\frac{-(s - x)^2}{4D_0 t}\right] - \exp\left[\frac{-(s + x)^2}{4D_0 t}\right]\right\} ds \tag{37}$$

and

$$f_2(x, t) = (4\pi D_0 t)^{-1/2} \times \int_0^t C_0(s) \exp\left[\frac{V_0^2 s}{4D_0} - \frac{x^2}{4D_0(t - s)}\right] (t - s)^{-3/2} ds . \tag{38}$$

If $C_0(t)$ and $Z_0(t)$ are constants, $C_0$ and $Z_0$, respectively, then the solution (36) reduces to

$$\frac{C(x, t) - Z_0}{C_0 - Z_0} = \frac{1}{2}\left[1 + \operatorname{erf}(\sqrt{a_1 q} - x\sqrt{a_2/q} + \exp\left(\frac{V_0}{D_0}\right) \operatorname{erfc}\ (\sqrt{a_1 q} + \sqrt{a_2/q})\right], \tag{39}$$

where q is the volume of the soil solution that has entered the soil column since time t = 0 and is given by

$$q = v_0 t\theta \quad ,$$

$a_1$ and $a_2$ are given by

$$a_1 = V_0/(4\theta D_0)$$

$$a_2 = \theta V_0/(4D_0),$$

and erf and erfc are the error and complementary error functions respectively.

When $C_0(t)$ is the step function given by

$$C_0(t) = \begin{cases} C_0 \ , & 0 \leq t \leq T \ , \\ C_\infty \ , & T < t \ , \end{cases} \tag{40}$$

the solution (36) reduces to

$$C(x, t) = \begin{cases} C_0 \ H(V_0\theta t) \ , & 0 \leq t \leq T \ , \\ C_0 \ H(V_0\theta t) + (C_\infty - C_0) \ H[V_0\theta(t - T)] \ , & T < t < +\infty \ , \end{cases} \tag{41}$$

where

$$H(v) = \frac{1}{2} \left[1 + \mathrm{erf}(\sqrt{q_1 v} - x\sqrt{a_2/v}) + \exp(V_0/D_0) \ \mathrm{erfc}(\sqrt{a_1 v} + x\sqrt{a_2/v})\right] . \tag{42}$$

For the special case $C_\infty = 0$, this solution has been used by Warrick et al. (1971) and Balasubramanian et al. (1976). Assuming initial conditions of the form

$$\begin{aligned} C(x, 0) &= 0, \quad x > 0 , \\ C(0, t) &= C_0, \quad t \geq 0 , \end{aligned} \tag{43}$$

then the solution (39) of Eq. (34) reduces to

$$\frac{C(x, t)}{C_0} = \frac{1}{2} \operatorname{erfc}\left[\frac{x - V_0 t}{(4\theta D_0 t)^{1/2}}\right] + \frac{1}{2} \exp \frac{V_0 x}{D_0} \operatorname{erfc}\left[\frac{x + V_0 t}{(4 D_0 \theta t)^{1/2}}\right]. \tag{44}$$

This form of the solution has been obtained by Rafai et al. (1956), Ogata and Banks (1961), and Elrick et al. (1966).

Davidson et al. (1968) found an analytic solution to Eq. (34) under the boundary conditions

$$\begin{aligned} &C(x, 0) = 0, \quad 0 \leq x , \\ &V_0\, C(0, t) - D_0 \frac{\partial C}{\partial x}(0, t) = V_0 C_0, \quad 0 \leq t \leq T , \\ &V_0\, C(0, t) = 0, \quad t > T . \end{aligned} \tag{45}$$

These boundary conditions simulate the agriculturally interesting problem of a uniform application of a solute solution (for example, a herbicide) to the surface of the soil for a time period T, after which solute-free water is applied and the solute slug is displaced through the soil. This type of application of a solute solution is called a pulse application.

A solution to Eq. (34) under the above boundary conditions was also reported by Lindstrom et al. (1967). Lai and Jurinak (1972a) used these solutions to study the dynamics of $Na^+$ and $Mg^{2+}$ transport

through Yolo loam soil at different pore velocities. They found that at high pore velocities, there was good agreement between theoretical and experimental retention curves. At lower pore velocities, however, the transport of cations was faster than predicted by the model.

Numerous other analytic solutions to Eq. (34) for a semi-infinite column and various initial conditions have appeared in the literature. See, for example, Banks and Ali (1964), Cho (1971), Cho et al. (1970), Ogata (1964, 1970), Ogata and Banks (1961), Brenner (1962), Gershon and Nir (1969), Villermaux and Van Swaaij (1969), Eldor and Dagan (1972), Lindstrom et al. (1967), Crank (1956), Marino (1974), Banks and Ali (1964), Kirda et al. (1973), and Warrick et al. (1971).

### 6.1.2 Finite column

Bastian and Lapidus (1956) obtained an analytic solution of Eq. (33) subject to the linear adsorption isotherm $S = K_d C$ which is applicable to solute transport in a column of finite length. In order to be able to find a solution of (34) for a finite column of length L, the behavior of the fluid phase at each end of the column must be described. The boundary conditions used by Bastian and Lapidus are given by

$$\begin{aligned} &V_0\, C(0, t) - D_0 \frac{\partial C}{\partial x}(0, t) = V_0 C_0, \quad t \geq 0 , \\ &\frac{\partial C}{\partial x}(L, t) = 0, \quad t \geq 0 , \\ &C(x, 0) = 0, \quad 0 \leq x \leq L , \end{aligned} \tag{46}$$

where $C_0$ is the initial concentration of the solute introduced to the column at time t = 0. The use of boundary conditions of this type has been discussed in detail by Wehner and Wilhelm (1956). These boundary conditions describe slug flow of the solute when D = 0 and perfect mixing of the solute in the soil matrix when $D = +\infty$.

Cleary and Adrian (1973) give an analytic solution applicable to solute transport in a finite column. The initial and boundary conditions they use are given by

$$
\begin{aligned}
&C(0, t) = C_0, \quad t \geq 0 , \\
&\frac{\partial C}{\partial x}(L, t) = 0, \quad t > 0 , \\
&C(0, x) = 0, \quad 0 \leq x \leq L ,
\end{aligned}
\tag{47}
$$

where $C_0$ is the concentration of the solute in the soil solution. Solutions similar to that given by Cleary and Adrian have been used by Gupta and Greenkorn (1973), Kirda et al. (1973), Lai and Jurinak (1972b), Warrick et al. (1971), Brenner (1962), Rose and Passioura (1971), and Bresler (1973).

Selim and Mansell (1976) give an analytic solution to Eq. (34) in a finite column subject to the boundary conditions

$$
\begin{aligned}
&C(x, 0) = C_i, \quad 0 \leq x \leq L , \\
&\frac{\partial C}{\partial x}(L, t) = 0, \quad t \geq 0 , \\
&V_0\, C(0, t) - D_0 \frac{\partial C}{\partial x}(0, t) = V_0 C_0, \quad 0 \leq t \leq T , \\
&V_0\, C(0, t) - D_0 \frac{\partial C}{\partial x}(0, t) = 0, \quad t \geq T ,
\end{aligned}
\tag{48}
$$

where $C_i$ is the initial solute concentration throughout the soil column and $C_0$ is the concentration of the applied solute solution. These boundary conditions describe a continuous application of a solute solution of constant concentration for a time period T, after which solute-free water is applied to the soil in other words, a pulse application. The case of a continuous solute application can be obtained as a special case of a pulse application by choosing T very large.

## 6.2 First-Order Kinetic Reversible Linear Model

We will now present an analytic solution of Eq. (33) subject to the first-order kinetic reversible linear adsorption equation

$$\frac{dS}{dt} = k_1 C - k_2 S \quad . \tag{49}$$

If we assume initial conditions of the form

$$\begin{aligned} C(x, 0) &= Z(t) \ , \quad x > 0 \ , \\ S(x, 0) &= N_0(t) \ , \quad x > 0 \ , \\ C(0, t) &= C_0(t) \ , \quad t \geq 0 \ , \end{aligned} \tag{50}$$

the solution given by Lapidus and Amundson (1952) is given by

$$C(x, t) = \exp\,[Vx/2D][Y_1(x, t) + Y_2(x, t)] \ , \tag{51}$$

where $Y_2$ is defined by the relations

$$Y_2(x, t) = \int_0^t \left[F'(s) + \frac{x}{\sqrt{D}} F(s)\right] C_0(t - s)\, ds \ , \tag{52}$$

$$F(t) = \exp\,(-k_2 t) \times \int_0^t I_0\,[2\sqrt{k_1 k_2 \theta s(t - s)/\rho}\,]\, \frac{x}{\sqrt{4\pi D s^3}} \exp\left(\frac{-x^2}{4Ds} - sd\right) ds \ , \tag{53}$$

$$d = V^2/4D + k_1\rho/\theta - k_2 \ , \tag{54}$$

and $Y_1$ is defined by the relations

$$Y_1(k, t) = \int_0^\infty \{[H'(t, x - s) - H'(t, x + s)]\ X(s) + [H(t, x - s) = H(t_1, x + s)]\ Y(s)\}\ ds \ , \tag{55}$$

$$H(t, q) = \sqrt{\frac{D}{\pi}} \exp(-k_2 t) \int_0^t I_0\left[2\ \frac{\sqrt{k_1 k_2 \rho s}}{\theta}\ (t - s)\right] \exp\left[\frac{-q^2}{4s} - sd\right] \frac{ds}{\sqrt{s}} \ , \tag{56}$$

$$X(s) = Z_0(s)\ \exp(Vs/2D)/D \ , \tag{57}$$

$$Y(s) = (k_2/2D)\ [N_0(s) + \frac{\theta}{\rho}\ Z_0(s)]\ \exp(Vs/2D) \ , \tag{58}$$

where $I_0$ is the modified Bessel function of zero order.

The complexity of the solution to Eq. (32) subject to the linear first-order kinetic adsorption equation (49) is characteristic of solute transport problems when any adsorption mechanism but the linear adsorption isotherm $S = K_d C$ is assumed. For the special case $C_0(t) = C_0$, $Z_0 = N_0 = 0$, Eq. (51) reduces to

$$C(x, t) = C_0\ \exp\ (Vx/2D)\ \ [\ F(t) + k_2 \int_0^t F(s)\ ds\ ] \ .$$

Numerous other analytic solutions of Eq. (33) subject to the linear first-order kinetic adsorption equation (49) and various initial conditions exist in the literature. See, for example, Horenstein (1945), Lindstrom and Boersma (1971a, 1971b), Lindstrom and Narasimhan (1973), Lindstrom and Stone (1974a, 1974b), Lindstrom and Oberhettinger (1975), Nielsen and Bigger (1962), Ogata and Banks (1961), Ogata (1964), Eldor and Dagan (1972), Oddson et al. (1970), Lindstrom (1976), Gupta and Greenkorn (1973), and Marino (1974).

### 6.3 Analytic Solution of the Cameron-Klute Model

In the Cameron-Klute combined equilibrium and kinetic model for adsorption, it was assumed that the total adsorption had two components, one governed by the linear adsorption isotherm,

$$S = k_3 \frac{\theta}{\rho} C \ , \tag{25}$$

and the other governed by the first order linear kinetic model,

$$\frac{\partial S}{\partial t} = k_1 \frac{\theta}{\rho} C - k_2 S \ . \tag{26}$$

Combining Eq. (25) with Eq. (26), one obtains

$$(1 + k_3) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \ , \tag{59}$$

where the kinetic component $\frac{\partial s}{\partial t}$ is given by

$$\frac{\partial S}{\partial t} = k_1 \frac{\theta}{\rho} C - k_2 S \ . \tag{60}$$

We will make the following dimensionless transformations:

$$\begin{aligned} &T = vt/L \ , \quad B = vL/4D \ , \quad \xi = x/L \ , \\ &C = C/C_0 \ , \quad N = \rho s/\theta C_0 \ , \quad N_1 = \rho s_1/\theta C_0 \ , \\ &K_1 = Lk_1/v \ , \quad K_2 = Lk_2/v \ , \quad K_3 = k_3 \ . \end{aligned} \tag{61}$$

The dimensionless time T is equivalent to the number of pore volumes that have passed through a column of length L. The Brenner number B is a measure of the relative importance of convective transport as compared with dispersion (Rose and Passioura 1971). The scaling parameter $C_0$ is chosen as the concentration of the incoming solute.

Substituting Eq. (61) into (59) and (60), we obtain

$$(1 + K_3) \frac{\partial C}{\partial t} = \frac{1}{4B} \frac{\partial^2 C}{\partial \xi^2} - \frac{\partial C}{\partial \xi} - \frac{\partial N_1}{\partial T} \ , \tag{62}$$

$$\frac{\partial N_1}{\partial T} = K_1 C - K_2 N_1 \ . \tag{63}$$

The initial conditions used are as follows:

$$\begin{aligned} &C(0, T) = 1 \ , \quad T > 0 \ , \\ &C(\xi, 0) = 0 \ , \quad \xi > 0 \ , \\ &N(\xi, 0) = 0 \ , \quad \xi > 0 \ , \\ &\lim_{\xi \to \infty} C(\xi, T) = 0 \ . \end{aligned} \tag{64}$$

The solution of (62) and (63) subject to (64) given by Cameron and Klute is

$$C(\xi, T) = \frac{2}{\pi^{1/2}} [\exp(2B\xi)] \int_{W}^{\infty} \exp[-h^2 - B^2\xi^2/h^2] \, J(x, t) \, dh \, , \qquad (65)$$

where

$$w = [B\xi^2 (1 + K_3)/T]^{\frac{1}{2}}$$

$$x = K_1 \, B\xi^2/h^2$$

$$y = K_2 \, [T - B\xi^2 (1 + K_3)/h^2]$$

and J(X, Y) is the J function defined by

$$J(X, Y) = 1 - e^{-y} \int_0^x e^{-t} \, I_0(2\sqrt{Yt}) \, dt \, .$$

The function J(X, Y) appears in a wide variety of problems, and therefore no attempt will be made to list its properties. The reader is referred to Luke (1962) or to the original work of Goldstein (1953). The total adsorbed concentration N of solute in the soil matrix is given by

$$N(\xi, T) = K_3C(\xi, T) + K_1 \int_0^T C(\xi, u) \exp[-K_2(T - u)]\, du \ , \tag{66}$$

where $C(\xi,T)$ and $C(\xi,u)$ are calculated from (6.5).

If $K_3 = 0$, Eq. (65) reduces to the dimensionless form of the solution obtained by Ogata (1964) for the first-order reversible kinetic model. If $K_2 = 0$, Eq. (65) reduces to

$$C(\xi, T) = \frac{1}{2} \{\exp[2B\xi(1 - M)] \operatorname{erfc}[\xi(B/T')^{1/2} - M(BT')^{1/2}]$$

$$+ \exp[2B\xi(1 + M)] \operatorname{erfc}[\xi(B/T')^{1/2} + M(BT')^{1/2}]\} \ , \tag{67}$$

where

$$M = (1 + K_2/B)^{1/2} \ ,$$

$$T' = T(1 + K_3) \ .$$

Equation (67) represents the solution to a combination equilibrium and first-order linear irreversible kinetic model. If $K_1$ and $K_2$ equal zero, this combination model reduces to the linear isotherm model solved in Sect. 6.1. The solution (36) can be obtained from Eq. (67) by setting $M = 1$.

## 6.4 Convolution Solutions

This section presents a solution, based upon the use of convolution integrals, of the one-dimensional equation describing the flow of a solute through an adsorbent soil. For simplicity, we assume that a linear adsorption isotherm describes the adsorption equilibrium between the soil and the soil solution. Thus, as in Sect. 6.1, Eq. (33) reduces to

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2} - V_0 \frac{\partial C}{\partial x} , \tag{68}$$

where

$$D_0 = D/\left(1 + \frac{\rho K_d}{\theta}\right),$$

$$V_0 = V/\left(1 + \frac{\rho K_d}{\theta}\right) .$$

The analytic solution of Eq. (68) corresponding to an instantaneous release of a finite quantity of material M ($g/cm^2$) is given by

$$C(x, t) = \frac{M}{\sqrt{4\pi D_0 t}} \exp\left[- \frac{(x - V_0 t)^2}{4D_0 t}\right] . \tag{69}$$

For a more general time-dependent release, the solution of (68) may be obtained by the use of a convolution integral. Assume that, instead of an instantaneous release of a finite quantity of material, the material is continuously introduced at the rate $\frac{dm}{dt} = f(t)$ [$g/(cm^2 \cdot sec)$]. The concentration distribution resulting from this continuous discharge is given by

$$C(x, t) = \frac{1}{\sqrt{4\pi D_0}} \int_0^T \frac{f(s)}{\sqrt{t - s}} \exp\left\{\frac{-[x - V_0(t - s)]^2}{4D_0(t - s)}\right\} ds . \tag{70}$$

From Eq. (70) the concentration distribution corresponding to a square pulse release of amplitude $C_0$ and duration $T_D$ is given by

$$C(x, t) = \frac{C_0}{\sqrt{4\pi D_0}} \int_0^{T_D} \frac{1}{\sqrt{t - s}} \exp\left\{\frac{-[x - V_0(t - s)^2]}{4D_0(t - s)}\right\} ds \tag{71}$$

for $0 \leq t \leq T_D$ and by

$$C(x, t) = \frac{C_0}{\sqrt{4\pi D_0}} \int_0^{T_D} \frac{1}{\sqrt{t - s}} \exp\left\{\frac{-[x - V_0(t - s)^2]}{4D_0(t - s)}\right\} ds \tag{72}$$

for $T_D \leq t$.

This equation may be integrated to give

$$\begin{aligned} C(x, t) &= \frac{C_0}{2V_0} \exp\left(\frac{V_0 x}{2D_0}\right) g(x, t) , \quad 0 < t < T_0 , \\ C(x, t) &= \frac{C_0}{2V_0} \exp\left(\frac{V_0 x}{2D_0}\right) [g(x, t) - g(x, t - T_D)] , \quad T_D < t , \end{aligned} \tag{73}$$

where

$$g(x, t) = \left[\operatorname{erf}\left(\frac{x + V_0 t}{\sqrt{4D_0 t}}\right) - 1\right] \exp\left(\frac{V_0 x}{2D_0}\right) - \left[\operatorname{erf}\left(\frac{x - V_0 t}{\sqrt{4D_0 t}}\right) - 1\right] \exp\left(- \frac{V_0 x}{2D_0}\right).$$

In general, for releases other than square pulses, the integral (70) must be evaluated by numerical quadrature.

## 7. CONCLUSION

This study provides a state-of-the-art review of selected aspects of the mathematical theory related to the transport of reactive solutes in soil. It focuses on two primary areas of interest: the mathematical models in current use for description of the adsorption-desorption process in soil and the known analytic solutions to the differential equations decribing the convective-dispersive transport of reactive

solutes in one dimension. It is expected that the review provided by this study will be of assistance in the development of improved methodologies for assessing health effects associated with the terrestrial transport of both radioactive and chemical pollutants from energy-related technologies.

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