

16

Solute Transport

16.1 INTRODUCTION

Water entering the soil profile from rain or irrigation is essentially a dilute solution. Rainwater is pure when it condenses to form clouds; during descent it absorbs atmospheric gases (i.e., CO₂, N₂, products of sulfur and O₂, etc.). When water flows on soil surface as overland flow and/or through the soil matrix, it also dissolves solutes (e.g., salts, fertilizers, pesticides). These solutes not only move with soil water but also within the soil matrix mainly due to the concentration gradients. Sometimes, solutes react among themselves and/or with soil material according to a range of physical and chemical processes.

In agricultural ecosystems, solutes may be categorized on the basis of their function (e.g., nutrients, pesticides, waste compounds, salts, organic chemicals, heavy metals, viruses, and bacteria). Understanding transport of solutes in soil is important to many management problems in agriculture. It can help when developing procedures for maximizing the effective use of fertilizers or pesticides and other chemicals within the root zone while minimizing their movement into groundwater. Knowledge of these processes is important to understanding the problems of contamination of natural water through leaching or redistribution within a vadose zone to groundwater, availability of solutes for plant uptake, surface runoff, salt intrusion in coastal aquifers, seepage from storage or disposal systems, and chemical residues.

Depending upon chemical stability and reactivity, the solutes are broadly classified into two categories: (i) conservative solutes, which remain unchanged physically and chemically, and do not undergo irreversible reactions, such as chloride (Cl) and bromide (Br); and (ii) nonconservative solutes, which can undergo irreversible reactions and change their physical or chemical phase. The nonconservative solutes can be divided into labile solutes and reactive solutes. The labile solutes can undergo reversible or irreversible physiochemical, biochemical, or microbial reactions and can change their physical or chemical phase with time. The examples of labile solutes are: nitrate, sulfate, and ammonia, which are involved in mineralization, immobilization, or redox reactions. Some pesticides are also labile and their lability is quantified by their half-life (White et al., 1998). Reactive solutes undergo reversible or irreversible reactions with soil constituents by way of adsorption (adsorption of cations, e.g., Ca⁺, Mg⁺⁺, on clay particles), precipitation or dissolution (e.g., precipitation of calcium as calcium sulfate or

calcium carbonate). The anions (e.g., such as nitrate (NO_3^-), Cl^- , and Br^-), which are weakly adsorbed on positively charged sites, are known as nonreactive solutes. The transport of reactive and nonreactive solutes through soil is affected relative to the movement of water (Nielsen et al., 1986).

Some solutes are already present in the water-filled pore space of the soil. These solutes may be present in the soil owing to: (i) mineralization of organic matter, (ii) saline groundwater intrusion, (iii) fertilizer and/or pesticide application, (iv) atmospheric deposition, and (v) weathering of mineral. When solute-free water flows through the soil matrix, the concentration of these preexisting solutes is the highest in those pores experiencing the lowest water flux. Apart from the preexisting, solutes are also applied on soil surface (e.g., fertilizer, pesticides, etc.). Basically solute transport within a soil matrix occurs by two physical processes: diffusion and convective flow. Several simple and complicated mathematical models have been developed in the past, which can reproduce the experimental results very well. Most of these models are developed for the macroscopic scale (Nielsen et al., 1986), although pore scale description is available (e.g., Navier–Stokes equation). This chapter describes the transport mechanisms in more detail and discusses the transport models on a macroscopic scale.

16.2 SOLUTE TRANSPORT PROCESS

The movement of solutes inside the soil matrix is caused by “mass flow” or “convection.” This type of flow is also called *Darcian flow* (see Chapter 12). The velocity at which solutes travel through soil matrix is generally known as “pore water velocity” and is the ratio of volumetric flow of solute through a unit cross-sectional area and volumetric moisture content of the soil matrix. In other words, the pore water velocity is the ratio of Darcian velocity and moisture content. In general, pore water velocity accounts for the straight-line length of path traversed in the soil in a given time. In reality, the flow paths are not always straight but are irregular or tortuous. This property is known as “tortuosity” of soil pores. Solute does not always flow with water but sometimes goes ahead of it due to the twin process of diffusion and dispersion or exclusion, lag behind due to adsorption or retardation, or get precipitated or volatilized. The movement of solute from the higher concentration to the lower concentration gradient is also known as the process of “diffusion.” This process commonly occurs within gaseous and liquid phases in the soil matrix due to the random thermal motion, also called “Brownian movement.” There is another simultaneous process that tries to mix and eventually even out the concentration gradients known as “hydrodynamic dispersion.” Diffusion is an active process, whereas dispersion is a passive process. However, in most practical applications these two solute transport processes are considered additive.

Some chemicals, which are soluble in water and have a nonnegligible vapor phase, can exist in three different phases in a soil matrix: as a dissolved solute in soil water, as a gas in soil air, and as an ion adsorbed on the soil organic matter or charged clay mineral surfaces. Therefore, all solute concentration terms are not equal in dimensions and depend on the concentration in these soil phases and the partitioning of these phases. The total solute resident concentration (C , g cm^{-3}) in a soil matrix can be mathematically expressed as

$$C = \rho_b C_a + \theta C_l + f_a C_g \quad (16.1)$$

where ρ_b is the soil bulk density (g cm^{-3}), C_a is adsorbed concentration (g g^{-1}), θ is volumetric soil moisture content ($\text{cm}^3 \text{cm}^{-3}$), C_l is dissolved solute concentration (g cm^{-3}), f_a is the volumetric air content ($\text{cm}^3 \text{cm}^{-3}$), and C_g is gaseous solute concentration (g cm^{-3}). Soil physical parameters (ρ_b , θ and f_a) weight the solute concentrations in the three phases of soil on a volume basis, and convert different reference dimensions to cm^3 of soil. The resident concentration is the volume-averaged concentration in soil, which is measured by extracting a known volume of soil in water. The resident concentration is expressed as the mass of solute per unit volume of soil water to make it comparable to flux-averaged concentration. The flux concentration is the solute concentration in water flowing through the soil.

16.3 MACROSCOPIC MIXING

Several different mechanisms operating in the porous media during transport of solute are responsible for the mixing at macroscopic level. Some of these include the following (Greenkorn, 1983):

1. *Molecular diffusion*: If the process is stationary or slow moving and the time required for the solute to move through the porous media is sufficiently long (i.e., for sufficiently long time scale) molecular diffusion is the primary source of macroscopic mixing.
2. *Tortuosity*. The tortuous flow paths inside the soil profile causes the fluid element to remain at different distances from the same starting position even when they travel at the same pore water velocity (ratio of Darcy velocity and soil moisture content).
3. *Connectivity of pores*: If the pores are not well interconnected or if some of the pores in the porous media are not accessible to the fluid element flowing through that pore, they cause macroscopic mixing and dispersion.
4. *Hydrodynamic dispersion*: The solute element near the wall of pore travels at a different velocity than the element at the center of pore (Fig. 16.1a). This results in a velocity gradient inside the pore and solute elements move relative to each other at different velocity.
5. *Immobile zones*: The immobile water zones normally causes the fluid element to move quicker and out in the effluent solution earlier (early breakthrough), and at the same time, increases the tail of the breakthrough curve mainly due to the slow release of solute element trapped inside immobile water (see Sec. 16.12).
6. *Turbulence*: If the size of the pore abruptly changes, the flow inside a pore may become turbulent and mixing is caused by eddies.
7. *Adsorption*: When the concentration front loses some ions abruptly as they are removed from solution by the process known as adsorption, the unsteady state flow occurs and the concentration profiles becomes flat.

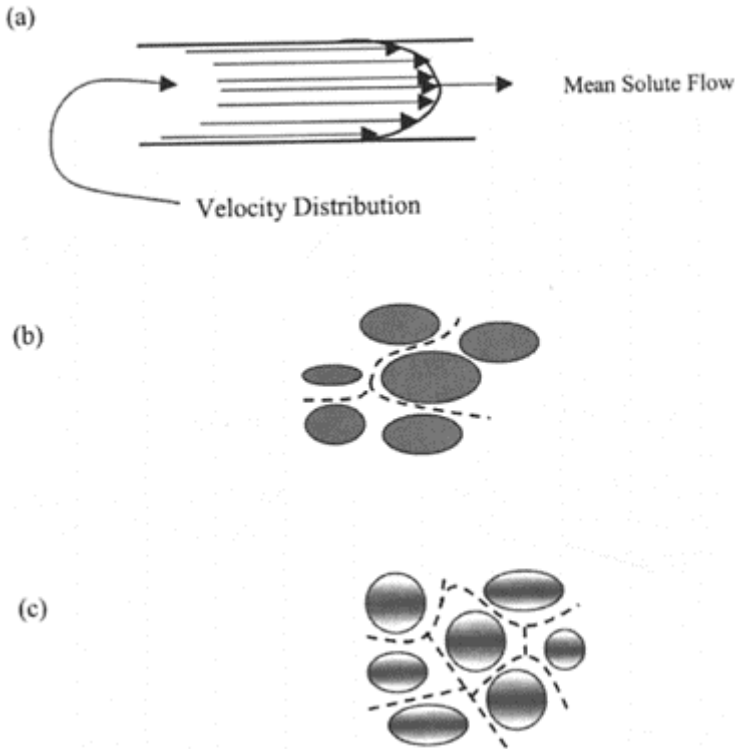


FIGURE 16.1 The physical mechanisms for hydrodynamic dispersion of solutes through soil matrix: (a) influence of velocity distribution within a soil pore; (b) influence of size of pore, and (c) influence of microscopic flow direction.

16.4 FICK'S LAW

There are two Fick's laws, which describe diffusion of substances in porous media. The movement of ions from areas of higher concentration to lower concentration is proportional to the concentration gradient, the cross-sectional area available for diffusion, and the elapsed time during the solute transport. The net amount of solute crossing a plane of unit area in unit time is known as the solute flux density (J ; $\text{gcm}^{-2}\text{s}^{-1}$), which is given by Eq. (16.2) known as Fick's first law (1855) for steady state one-dimensional solute transport:

$$J = -D_m \frac{\partial C}{\partial x} \quad (16.2)$$

where D_m is the ionic or molecular diffusion coefficient of the porous media (cm^2s^{-1}), C is the solute concentration (gcm^{-3}) and x is the distance (cm). The concentration gradient ($\partial C/\partial x$) in Eq. (16.2) is the driving force and the minus sign indicates that solute moves from areas of higher concentration to lower concentration. The molecular diffusion coefficient in Eq. (16.2) varies with soil physical and chemical properties of soil and solute (i.e., soil texture, soil moisture content, solute concentration, and pH), soil solute interactions, and temperature. The solute concentration follows a normal, or Gaussian, distribution and can be described by the mean and variance. The depth of penetration (X_p) of a diffusing ion in soil for a given time duration (t) can be estimated by the root mean-square displacement as follows:

$$X_p = (2D_m t)^{1/2} \quad (16.3)$$

Diffusion in soils is a relatively slow process and operates over small distances, thus maintaining the electrical neutrality of ions. For transient state condition, Eq. (16.2) is coupled with the one-dimensional mass conservation equation with no production or decay taking place during solute transport through soil

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \quad (16.4)$$

Equation (16.4) implies that the net change in solute concentration is as a result of net change in rate of flow. Combining Eqs. (16.2) and (16.4) and assuming that D_m is independent of solute concentration and depth, results in Fick's second law for one-dimensional transient solute flow

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial x^2} \quad (16.5)$$

16.5 TRANSPORT EQUATIONS

When a solute enters a soil matrix (which can be in a soil core, repacked soil column, or agricultural soil in a field) the initial sharp boundary between the resident and displacing solute starts diminishing mainly due to the twin processes of diffusion and dispersion. The transport of a solution through soil matrix consists of three main components: convection, diffusion, and dispersion, which are briefly described below.

16.5.1 Convection or Mass Transport

Convective or advective transport of a solution inside a soil matrix is known as the passive movement with flowing soil water. If the transport process has only convective transport without any diffusion, the water and solute move at the same average flow rate. Mathematically convective transport (J_m) can be expressed as

$$J_m = q_s C \quad (16.6)$$

where J_m is the flux density for convective or mass transport ($\text{ML}^{-2}\text{T}^{-1}$), q_s is the volumetric fluid flux density with dimensions of velocity (LT^{-1}), and C is the volume averaged solute concentration (ML^{-3}). The flux density of water can be calculated by the Darcy equation for a steady state flow of water. The q_s is also analogous to θ , where v is the pore water velocity (LT^{-1}).

16.5.2 Diffusive Transport

Diffusion is a spontaneous process resulting from the random thermal motion of dissolved ions and molecules. In general, the diffusion is an active process and diffusive transport tends to decrease the existing concentration gradients and moves the process towards homogeneity rather rapidly. Fick's law defines the diffusive transport and for one-dimensional steady state transport is given as:

$$J_D = -D_m \frac{\partial C}{\partial x} \quad (16.7)$$

where J_D is solute flux density for diffusive transport of solute ($\text{ML}^{-2}\text{T}^{-1}$), θ is the volumetric moisture content (L^3L^{-3}). The diffusion coefficient in soils (D_m) is slightly less than the diffusion coefficient in pure water (D_0) mainly due to the tortuous flow paths in soils.

$$D_m = D_0 \theta \xi \quad (16.8)$$

where ξ is the dimensionless tortuosity factor ranging roughly from 0.3 to 0.7 for most soils.

16.5.3 Dispersive Transport

The soil matrix consists of pores of different shapes, sizes, and orientation. This heterogeneity of pore structure causes a large deviation of local pore water velocities inside each individual pore. Consider a one-dimensional flow through a single capillary tube of constant radius R . According to Poiseuille's law, the flow rate through each pore varies proportional to the fourth power of the radius R (Kutilek and Nielsen, 1994). However, the flow velocity (v) through the tube is a decreasing function of radial distance (r) from the center of tube. If average velocity is v' then $v = 2v'(1 - (r^2/R^2))$, when $r=R$, i.e., at the wall of pore $v = 0$, and at $r=0$, i.e., at the center of pore $v = 2v'$. It is, therefore, clear that microscopic scale variations of pore water velocity in the soil matrix are very important and large.

Dispersive transport occurs because of the velocity variations in soil matrix with respect to average pore water velocity. The velocity variations in a soil matrix is caused by several factors such as zero velocity at the particle surface, which increases gradually and is the maximum at the center of pore or at air water interface under unsaturated

conditions (Fig. 16.1a). Pore sizes also create velocity gradients with the velocity in larger pores greater than the velocity in smaller pores (Fig. 16.1b). The other possible reason is the fluctuation of flow paths of an element of water with respect to the mean direction of flow (Fig. 16.1c). Macroscopically, dispersion process is similar to the diffusion process, however, unlike diffusion, it occurs only during water movement. Field and laboratory experiments have shown that the dispersive transport can be described by an equation similar to diffusion as follows:

$$J_h = -\theta D_h \frac{\partial C}{\partial x} \quad (16.9)$$

where D_h is the mechanical dispersion coefficient (Bear, 1972) and is assumed to be a function of fluid velocity as follows:

$$D_h = \lambda v^n \quad (16.10)$$

where λ is the dispersivity and exponent "n" is an empirical constant generally assumed equal to 1.

The mixing or dispersion that occurs along the direction of flow path is called longitudinal dispersion and that in the direction normal to flow is known as transverse dispersion. Diffusion is an active process whereas dispersion is passive, in spite of this, most analysis on solute transport considers both processes to be additive because macroscopically both processes are similar.

$$D = D_m + D_h \quad (16.11)$$

where D is the longitudinal hydrodynamic dispersion coefficient (Bear, 1972) or apparent dispersion coefficient (Nielsen et al., 1972).

Combining Eqs. (16.6), (16.7), (16.9), and (16.11) leads to the following expression for solute flux, J_s

$$J_s = -\theta D \frac{\partial C}{\partial x} + qC \quad (16.12)$$

The equation of continuity states that:

$$\frac{\partial J_s}{\partial x} = -\frac{\partial}{\partial t} (\theta C + \rho_b S_s) \quad (16.13)$$

where S_s is adsorbed concentration (MM^{-1}), ρ_b is the bulk density (ML^{-3}), and t is time (T). Combining Eqs. (16.12) and (16.13) gives the following solute transport equation

$$\frac{\partial}{\partial t} (\theta C + \rho_b S_s) = \frac{\partial}{\partial x} \left(\theta D \frac{\partial C}{\partial x} - qC \right) \quad (16.14)$$

It is well known that adsorption and exchange processes are usually nonlinear and also depend on the competing species in the soil system. Still, one of the most common approaches to describe the relationship between adsorbed and solution concentrations has

been to assume instantaneous adsorption and linearity between C and S of the form (forcing the constant or intercept to zero)

$$S_s = K_D C \quad (16.15)$$

where K_D is the empirical distribution coefficient. Inserting Eq. (16.15) into Eq. (16.14) and dividing both sides with θ results in Eq. (16.16):

$$\frac{\partial}{\partial t} \left(C + \frac{\rho_b K_D C}{\theta} \right) = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} - \frac{q}{\theta} C \right) \quad (16.16)$$

Assuming that the soil profile is homogeneous and moisture content and flux density are constant in time and space, Eq. (16.16) reduces to

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (16.17)$$

where R is the retardation factor and is given by

$$R = 1 + \frac{\rho_b K_D}{\theta} \quad (16.18)$$

K_D in Eq. (16.15) can be obtained from the slope of sorbed concentration (MM^{-1}) versus solution concentration (ML^{-3}). A zero value of K_D in Eq. (16.18) reduces R to 1, which indicates no interactions between solute and soil. A negative value of K_D makes R less than one, which indicates anion exclusion or immobile water, which does not contribute to convective transport. In case of anion exclusion, $(1-R)$ is known as anion exclusion volume. A positive K_D results in $R > 1$, which indicates sorption.

16.6 BREAKTHROUGH CURVES

When a fluid (or solute) is passed through a soil matrix containing another liquid in its pore space, the introduced fluid, which can also be called the displacing liquid or applied liquid, gradually displaces the preexisting liquid (displaced liquid). Analysis of the collected effluent from soil matrix at a given depth (or from one end of a repacked soil column) shows a change in composition of effluent solution with respect to time. If the displacing and displaced solutions are not mutually soluble, the process is called “immiscible” displacement (e.g., oil and water). On the other hand, if both solutions are soluble, the process is called “miscible” displacement (e.g., aqueous solutions). The graphical representation of the concentration of these solutes with respect to time or cumulative effluent volume or pore volume is known as “breakthrough curves” (BTC). Pore volume is the ratio of cumulative effluent volume (cm^3) at a specified time and total volumetric moisture content of soil (cm^3). Pore volume is a nondimensional number and is zero at time zero.

16.6.1 Solute Input

As is evident in Figs. 16.2a–c, BTCs can have different shapes depending upon the solute application. Figure 16.2a shows a BTC where effluent solute concentration increases and reaches a maximum and then remains constant thereafter. The y-axis on Fig. 16.2 is the relative solute concentration (C/C_0), which is the ratio of concentration of effluent solute collected at a given time (C) and the concentration of displacing or incoming solution (C_0). The BTC in Fig. 16.2a is for a step input of displacing solute or tracer, where applied solution displaces all the preexisting solution gradually.

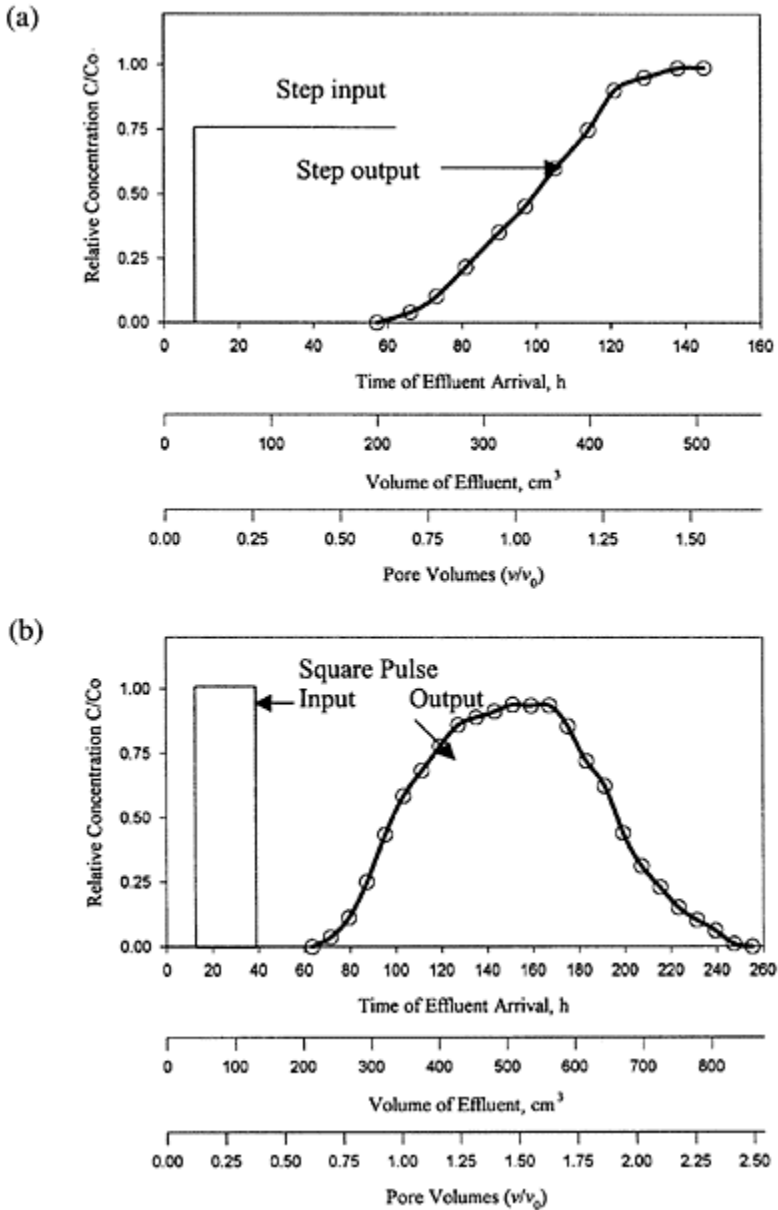
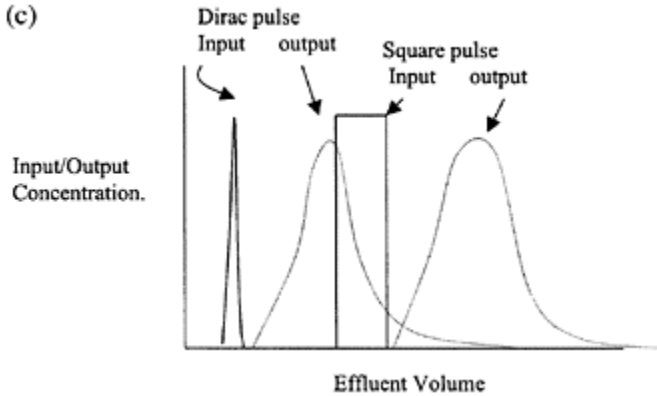


FIGURE 16.2 Breakthrough curves with respect to time of effluent arrival, volume of effluent, and pore volumes, (a) Chloride application as a step input through a 10 cm loam soil column

(pore water velocity= 0.11 cm.h^{-1}); (b) chloride application as a pulse input through a 10 cm loam soil column (pore water velocity= 0.1 cm.h^{-1}); and (c) schematic for a Dirac and square pulse input and output. (Modified from Shukla et al., 2002.)



Therefore, the concentration of applied solution increases whereas that of the preexisting solution decreases with time. If the application of displacing or applied solution continues, it attains the maximum concentration equal to C_0 . The ETC in Fig. 16.2b is obtained from a predetermined volume of the displacing solution followed by the original or preexisting solution. This type of solute application is known as “pulse” application. A pulse application can be: (i) a distributed pulse, (ii) a dirac pulse, and (iii) a square pulse. The concentration of solution applied as a distributed pulse gradually increases, attains a maximum, and then gradually goes down to zero (Fig. 16.2b). A solute pulse application for an infinitesimally short period is known as a “dirac pulse” (Fig. 16.2c). When time for solute pulse application is much smaller than time of leaching, it is called a dirac pulse input (e.g., single application of highly soluble fertilizer, pesticide, etc.). A square pulse is a step-up change followed by a step-down change, and the ETC shows a steep rise followed by steep fall (Fig. 16.2c).

16.6.2 Some Interpretations of Breakthrough Curves

Pore volumes are defined as the ratio of the volume of displacing water (V , water entered or flowed out at a given time), and the volumetric moisture content of the soil (V/V_0). Assuming that the moisture content of soil in a repacked column is $0.5 \text{ cm}^3 \text{ cm}^{-3}$ (or 50%) and the total volume of soil column is 100 cm^3 , therefore, volumetric moisture content of the repacked soil column is 50 cm^3 . Once 50 cm^3 of displacing solution is passed through the soil column, it corresponds to a pore volume of 1.

Soil–Solute Interactions

The ETC in Fig. 16.3a depicts a condition when a solute of a given concentration displaces another solute (such as water) in such a way that all the soil pores start contributing at the same time and the solute concentration jumps from zero to the maximum (C_0) as soon as 1 pore volume of displacing solution passes through the soil column. This type of flow is known as a “piston flow,” which corresponds to pure mass flow or convection. In piston flow the entire center of solute front arrives at the end of column at the same time. Piston flow occurs in the absence of diffusion or dispersion or any type of interactions between solute and soil and solute and water move at the same velocity inside soil matrix. This type of flow is rare or near impossible under natural conditions. For known moisture content of soil and column dimensions, it is possible to calculate the number of pore volumes required before piston flow begins. The time required for a displacing solute to reach the other end of a column is known as breakthrough time, residence time, or travel time (t^*), and is equal to L/v , where L is the length of soil column. For sorbing solutes the total travel time is obtained by multiplying R and L/v .

The ETC in Fig. 16.3b shows an early arrival of displacing solute in the effluent solution (less than 1 pore volume). This process takes place because of the difference in the velocity at which water and solute travel inside the soil domain. The solute travels ahead of water because of “molecular diffusion and hydrodynamic dispersion.” The ETC presented in Fig. 16.3b passes through C/C_0 of 0.5 at pore volume of 1. The area A and area B of this figure are numerically equal. This ETC represents a “convective dispersion process” with no interaction between solute and soil. The ETC in Fig. 16.3c is slightly shifted or retarded towards the x-axis. This type of shift is known as “sorption.” Opposite of sorption is “repulsion” or a phenomenon of “anion exclusion” when ETC moves away from x-axis (Kutilek and Nielsen, 1994) (Fig. 16.3d).

Influence of Displacement Length

With increasing displacement length, the tortuosity and pore size distributions of the soil also increases. For a given pore water velocity, the total resident time of the solute in the soil increases with increasing displacement length. Therefore, the total mixing by convection and diffusion also increases (Nielsen and Biggar, 1962). Figure 16.4 makes it abundantly clear that if a pulse of same amount is passed through soil columns of 10, 20, and 30 cm length, the progressive attenuation of the initial concentration takes

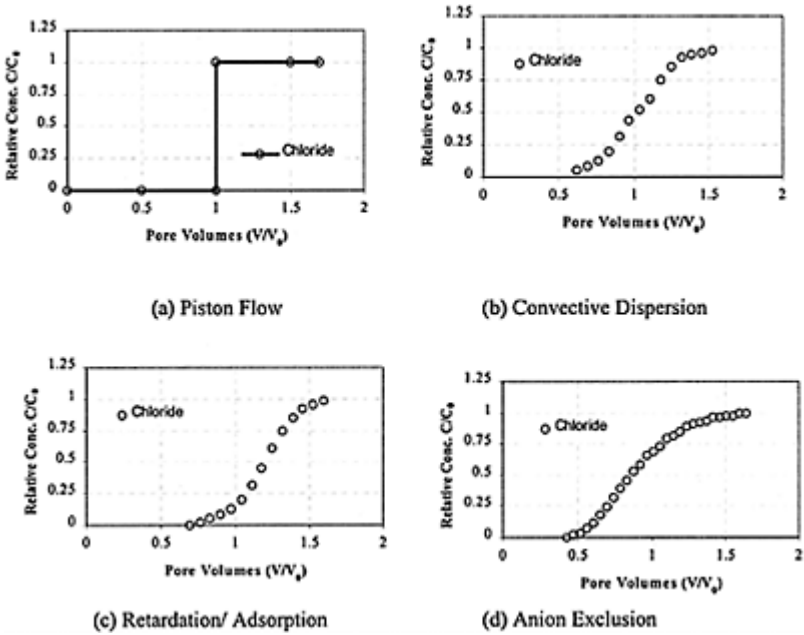


FIGURE 16.3 Interpretations from experimental breakthrough curves. (Modified from Kutilek and Nielsen, 1994; Shukla et al., 2002.)

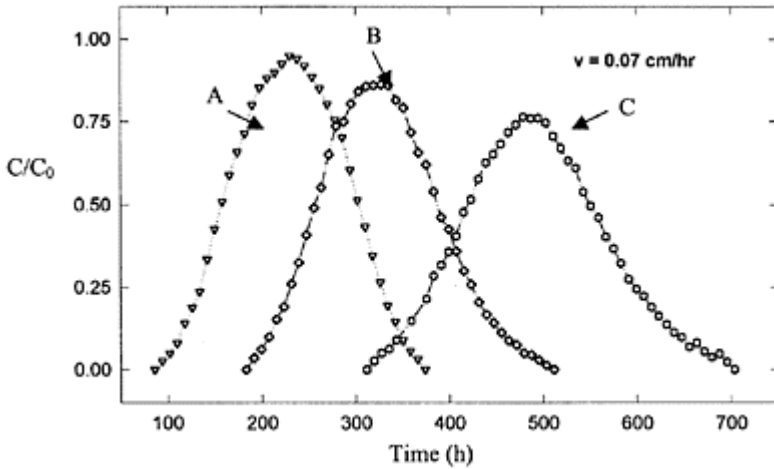


FIGURE 16.4 The progressive attenuation of BTCs for 10 cm (A), 20

cm (B), and 30 cm (C) soil columns for a pulse type chloride application through laboratory soil columns. (Redrawn from Shukla et al., 2000.)

place. This attenuation is the direct result of dilution. Therefore, solute applied as a pulse cannot carry its total mass beyond a certain depth. The total volumes of solution and total time required to completely displace the applied pulse increases with displacement length (Kutilek and Nielsen, 1994) (Fig. 16.4).

16.7 DISPERSION PROCESSES

Assuming the random capillary bundle concept (see Chapter 12), the classical dispersion theory was developed and a dispersion equation was suggested, which is similar to Fick's law and takes into account both dispersive and diffusive fluxes (Taylor, 1953; De Josselin De Jong, 1958; Bear and Bachmat, 1967; Fried and Combarous, 1971). There are several mechanisms that cause macroscopic mixing and are generally accounted for in the dispersion coefficient. Some of them are mixing due to tortuosity, inaccessibility of pore water, recirculation due to flow restrictions, macroscopic and hydrodynamic dispersion, and turbulence in flow paths (Greenkorn, 1983). In addition, molecular diffusion, the presence of dead-end pores, sorption, exclusion, and physical nonequilibrium affect the degree of asymmetry in BTCs in different proportions (Nielsen et al., 1986).

The hydrodynamic dispersion coefficient (D) is proportional to the pore water velocity of a solute under steady state flow conditions (Biggar and Nielsen, 1967; Bear, 1972).

$$D \propto \frac{q}{\theta} \text{ or } v \quad (16.19)$$

$$D = \lambda v$$

$$(16.20)$$

The proportionality constant, A , in Eq. (16.20) is known as dispersivity. The value of dispersivity depends upon the scale over which water flux and solute convection is averaged. Dispersivity is also dependent on the moisture content of the porous media (Krupp and Elrick, 1968) and decreases rapidly as moisture content decreases from saturation. A 10-fold increase in longitudinal dispersivity is reported when moisture content decreases from saturation (Wilson and Gelhar, 1974). Some typical values of dispersivity for laboratory soil columns range from 0.5 to 2 cm (Jury et al., 1991), 0.11 to 0.37 cm (for loam soil) and 0.14 to 0.22 cm (for sandy loam soil; Shukla et al., 2003). The dispersion processes are site specific and depend upon the subtler factors, which are related to the experimental conditions (Flury et al., 1998). The longitudinal dispersivity values are measured in field soils by placing a suction cup at different depths and measuring solute breakthrough as a function of time. The dispersivity calculated for field soils by one-dimensional convective dispersion Eq. (16.23) or method of moments (Jury and Roth, 1990) are given in Table 16.1.

TABLE 16.1 Dispersivity Values Measured in Field Soils Using Suction Cups

Soil	Tracer	Application rate, cm ^d ⁻¹	Dispersivity cm	Reference
Clay, silty clay	Cl, Tritium	2	9.4	Van de Pol et al. (1977)
Clay loam	Cl, NO ₃	–	8.3	Biggar and Nielsen (1976)
Clay loam	Br	96	5.2–23	Fleming and Butters (1995)
Clay loam	Br	30, 33, 41, 67	16–38	Jaynes (1991)
Loam	Cl	9.6–19.2	29	Roth et al. (1991)
Loamy sand	Br	1.1	3.2–15.8	Butters et al. (1989)
Loamy sand	Cl, NO ₃ , BO ₃	1.3	1–2	Ellsworth et al. (1996)
Sand	Cl	84	0.7–1.6	Hamlen and
		132	0.8–2	Kachanowski (1992)
Sand	Cl	84, 117	17, 2.7	Van Wesenbeck and Kachanowski (1991)

Source: Modified from Flury et al., 1998.

16.8 RELATIONS BETWEEN DISPERSION COEFFICIENT AND PORE WATER VELOCITY

The effective dispersion coefficient generally varies with mean microscopic flow velocity. Based upon the magnitude of the Peclet number (P , defined as vL/D , where L is a characteristic length), within the range of average pore water velocities, molecular diffusion dominates the dispersion of the solute at smaller displacement velocities and gives way to convective dispersion at greater velocities. Hence, for relatively small average pore water velocities we expect the apparent diffusion coefficient to have values close to that of the diffusion coefficient (D_0) in the soil solution, and to be only somewhat dependent on pore water velocity. At relatively large velocities, the dispersion coefficient is strongly related to pore water velocity.

The five dispersion regimes can be identified in Fig. 16.5 as (i) pure molecular diffusion; (ii) molecular diffusion and kinematic dispersion; (iii) predominant kinematic dispersion and (iv) and (v) as pure kinematic dispersion regimes (Shukla et al., 2002). In regimes ii-v, an increase in average pore water velocity increases mixing and reduces the impact of molecular diffusion in the direction of flow. Using mixing cell approximations, it can be shown that in the region $0.01 < P < 50$, dispersion is directly proportional to pore water velocity (Perkins and Johnston, 1963). Further

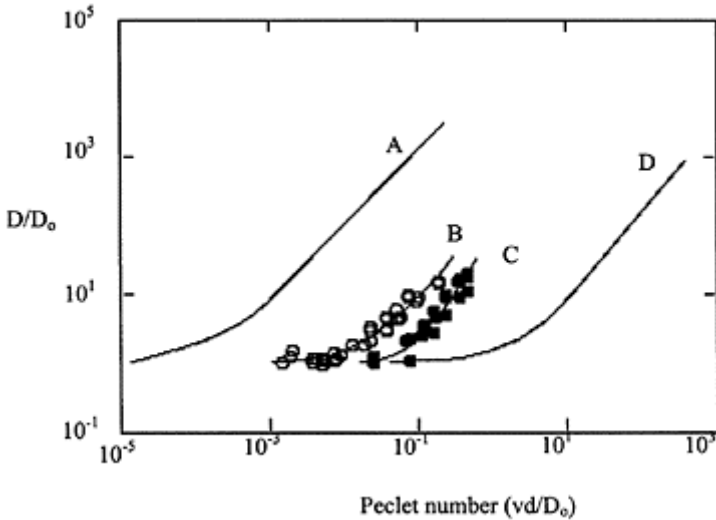


FIGURE 16.5 The relationship between DD_0^{-1} and Peclet number for: (A) field soil (A) (from Biggar and Nielsen, 1976), (B) loam, (C) sandy loam (from Shukla et al., 2002), and (D) single grain material (from Pfannkuch, 1963). (Redrawn from Shukla et al., 2002.)

increases in P results in a nonlinear relation to velocity ($P \propto v^n$, with $n > 1$). Pfannkuch (1962) and Torelli and Scheidegger (1972) reported an n value of 1.2, Taylor (1953) of 2, Biggar and Nielsen (1976) of 1.11, and Shukla et al. (2002) of 1.71 for sandy loam and 1.21 for loam.

The relations between D/D_o and Peclet number (vd/D_o) given as solid lines in Fig. 16.5 for natural undisturbed field soil by Biggar and Nielsen (1976), and for laboratory columns of loam and sandy loam soils (Shukla et al., 2002) and for graded sands and other single-grained materials (Pfannkuch, 1962) satisfy Eq. (16.21)

$$\frac{D}{D_o} = 1 + m \left(\frac{vd}{D_o} \right)^n \quad (16.21)$$

where

$$D_o = 0.66\theta D_m \quad (16.22)$$

with D_m being the diffusion coefficient for free solution. The D_o in Eq. (16.22) can be obtained from known values of θ and D_m (see also Chapter 18). For loam and the sandy

loam soils D_0 is 0.0222 and 0.0216 $\text{cm}^2 \text{h}^{-1}$, respectively (Shukla et al., 2002). Other reported values of D_0 in literature are: 0.02 $\text{cm}^2 \text{h}^{-1}$ by Jury et al. (1991), 0.01 $\text{cm}^2 \text{h}^{-1}$ by Sposito (1989), and 0.0203 $\text{cm}^2 \text{h}^{-1}$ by Shukla et al. (2003). The values of m increase with decreasing values of average particle diameter d while values of n range between 1 and 2 (Table 16.2). In the loam and sandy loam soils as well as the field soil, decreasing average particle diameter (increasing clay content) is associated with soil structure. The loam has relatively large pores as a result of microaggregates, and the sandy loam, although containing less clay than the loam, nevertheless has large pores also associated with its microaggregates as well as those associated with its high sand content. The field soil manifests the greatest value of m because of its large pore size distribution owing to its high clay content, its aggregation and its natural field structure.

16.9 MATHEMATICAL REPRESENTATION OF THE SOLUTE TRANSPORT PROCESS

The simplest form of one dimensional convective-dispersive equation (CDE), assuming macroscopic steady state water flow, constant soil–moisture content, and no interactions between the chemical and the solid

TABLE 16.2 Parameters for Eq. (21) for the Results Illustrated in Fig. 16.5

Soil	m	n	d mm	D_0 $\text{cm}^2 \text{h}^{-1}$
Laboratory columns (mostly sand) (Pfannkuch 1962)	0.5	1.2	0.156	0.022
Sandy loam (Shukla et al. 2001)	70.5	1.71	0.0508	0.0216
Loam (Shukla et al. 2001)	141	1.21	0.0158	0.0222
Field soil (more clay) (Biggar and Nielsen 1976)	17780	1.11	0.00272	0.0250

phase was developed by Lapidus and Amundson, (1952), which is similar to Eq. (16.17), for $R=1$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (16.22)$$

One additional term is added to Eq. (16.23) when chemical adsorption is included. Following is the one-dimensional solute transport equation describing transport through a homogeneous medium during steady state flow with adsorption [same as Eq. (16.17)]

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S_s}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (16.24)$$

The solution of Eq. (16.24) depends upon the knowledge of the relationship between adsorbed concentrations, S_s , and the solution concentration, C . Adsorption or exchange reactions perceived as instantaneous are described by equilibrium isotherms $S_s(C)$, which

can be of the mass action, linear, Freundlich, Langmuir, or any other functional form (Nielsen et al., 1986). Besides adsorption, the reactive process such as first-order degradation and zero-order production can also be taken into account during miscible displacement process. Therefore, the comprehensive CDE for one-dimensional transport of reactive solutes, subject to adsorption, first-order degradation, and zero-order production, in a homogeneous soil, is

written as:

$$\frac{\partial}{\partial t}(\theta C_r + \rho_b S_s) = \frac{\partial}{\partial x} \left(\theta D \frac{\partial C_r}{\partial x} - v C \right) - \theta \mu_\ell C_r - \rho_b \mu_s S + \theta \gamma_\ell(x) + \rho_b \gamma_s(x) \quad (16.25)$$

where C_r is the volume-averaged or resident concentration of liquid phase (ML^{-3}), S_s is the concentration of the adsorbed phase (MM^{-1}), v is the volumetric water flux density (LT^{-1}), μ_ℓ and μ_s are first-order decay coefficients for degradation of the solute in the liquid and adsorbed phases respectively (T^{-1}), γ_ℓ ($\text{ML}^{-3}\text{T}^{-1}$), and γ_s ($\text{MM}^{-1}\text{T}^{-1}$) are zero-order production terms for the liquid and adsorbed phases, D , θ , ρ_b , x , and t are the same as defined above. Assuming reversible equilibrium adsorption [Eq. (16.16)] and steady state flow in a homogeneous soil, Eq. (16.25) is modified to:

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} - \mu C_r + \gamma(x) \quad (16.26)$$

where μ and γ are combined first- and zero-order rate coefficients

$$\mu = \mu_\ell + \frac{\rho_b K_D}{\theta} \quad (16.27)$$

$$\gamma(x) = \gamma_\ell(x) + \frac{\rho_b \gamma_s(x)}{\theta} \quad (16.28)$$

16.10 SORPTION PHENOMENON

Adsorption is a process where ions or molecules are attached to the surfaces of soil solids. This results in a higher concentration of solute at the surface of solid phase than in the bulk solution. The opposite of adsorption is anion exclusion where concentration in a soil solution is higher than the solid phase. Sorption and exclusion processes are important in modifying the movement of chemicals through a soil domain. The plot between amount adsorbed and the amount in solution is known as the adsorption isotherm (Fig. 16.6). The forces active at soil-water interface and at molecular level are electrical and are the same at both levels. These forces vary as the reciprocal of the separation distance raised to a power. Equilibrium sorption (Fig. 16.6) of organic molecules is dominated by the organic fraction of soil.

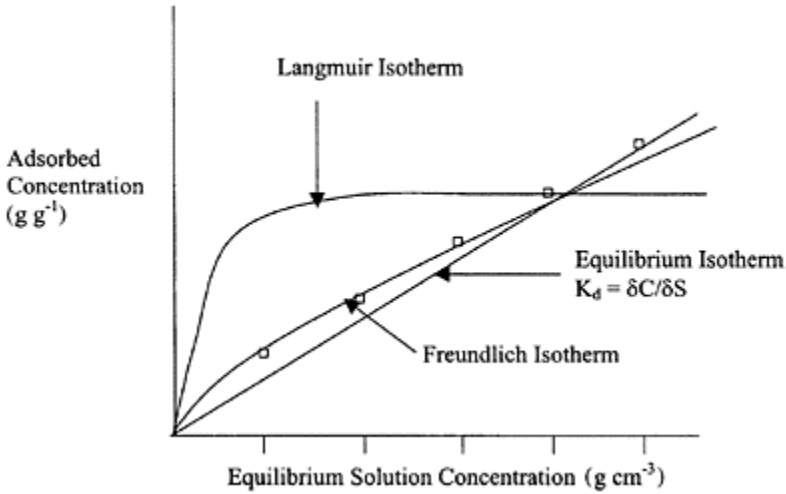


FIGURE 16.6 A schematic of adsorption isotherms. (Modified from July et al., 1994)

To account for this effect, value of K_D [Eq. (16.15)] is divided by soil organic carbon content (SOC) as below:

$$K_D = \text{SOC} * f_{oc} \quad (16.29)$$

The Freundlich adsorption model is given as $S_s = K_D C_1^n$, where n is close to 1 (Fig. 16.6). The Freundlich model is based on the assumption that there is no limiting concentration of adsorbate as solution concentration is increased without limit. This is unrealistic because available surfaces in soil domain are limited for adsorption to occur. The Langmuir adsorption model was developed from kinetics of gas adsorption on solid surfaces and has a sound conceptual basis. The model assumes that the energy of adsorption is constant and independent of surface coverage, the adsorbed molecules do not interact with each other, and the maximum possible adsorption is that of a complete monolayer (Fig. 16.6). The equilibrium adsorption (S_s) by Langmuir model is as follows:

$$S_s = \frac{aQC_1}{1 + aC_1} \quad (16.30)$$

where a is the ratio of adsorption rate constant, Q is the total number of available adsorption sites, and C_1 is the solute concentration in solution. Several sorption models are available in literature, some are derived from the adsorption of gases by solids while others are either empirical or kinetic.

Based upon multireaction approach, Selim (1992) proposed a model that involves three types of sites during sorption. The first type of site is equilibrium (S_{se}), where equilibrium between the sorbed and solution phases is established quickly. The second

type of sites is kinetic, S_{sk} , where adsorption is considered time dependent, and the third type-site is subjected to irreversible retention S_{sir} . Total amount of sorption can be described by the following relationship

$$S_s = S_{se} + S_{sk} + S_{sir} \quad (16.31)$$

Some of the equilibrium and kinetic sorption relationships are presented in Table 16.3.

16.11 EQUILIBRIUM ANION EXCLUSION MODEL

Certain anions interact with the negatively charged solid surfaces of the soil (such as clay or ionizable organic matter) and are excluded from the liquid region adjacent to the soil particle surfaces. This phenomenon is known as anion exclusion or negative adsorption. Eq. (16.17) represents the anion exclusion phenomenon for $R < 1$. In the presence of a soil solution, the negative charge extends from the surfaces of particles into the solution and forms diffuse double layer (Bolt, 1979). The existence of the negative charge causes repulsion of anions from this region. The resulting concentration gradient reduces the concentration of anion at the soil surface to zero, which increases exponentially with distance and at the limit of diffuse double layer becomes equal to the concentration of bulk solution (Bolt, 1979). Assuming that effective exclusion volume (θ_{ex}) expressed as volumetric moisture content is evenly distributed over the particle surface, the one-dimensional transport of an anionic solute exhibiting anion exclusion can be described as follows (Bresler, 1973; James and Rubin, 1986)

$$(\theta - \theta_{ex}) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - q \frac{\partial C}{\partial x} \quad (16.32)$$

The observed concentration (C) is less than the concentration of bulk solution (C_0) because of the exclusion volume, which does not contain ions. This interrelationship between C and C_0 can be expressed as follows:

$$C = C_0 \left[1 - \frac{\theta_{ex}}{\theta} \right] \quad (16.33)$$

TABLE 16.3 Equilibrium and Kinetic Models for Sorption in Soils^a

Model	Formulation
EQUILIBRIUM TYPE	
Linear	$S_{se} = K_D C_l$
Freundlich	$S_{se} = K_D C_l^n$
General Freundlich	$S_s / S_{smax} = [\omega C / (1 + \omega C)]^\beta$
Rothmund-Kornfeld ion exchange	$S_{si} / S_{sT} = K_D (C_i / C_T)^n$

Langmuir	$S_s/S_{smax}=(\omega C)^\beta/\omega C$
General Langmuir-Freundlich	$S_s/S_{smax}=(\omega C)^\beta/(1+\omega C)^\beta$
Langmuir with sigmoidicity	$S_s/S_{smax}=(\omega C)/(1+\omega C+\omega/C)$

KINETIC TYPE

First order	$\partial S_s/\partial t=K_D(\theta/\rho_b)(C_l-KD_1S_s)$
<i>n</i> th order	$\partial S_s/\partial t = K_D(\theta/\rho_b)(C_l^n - K_{D1}S_s)$
Irreversible (sink/source)	$\partial S_s/\partial t=K_D(\theta/\rho_b)(C-C_p)$
Second-order irreversible	$\partial S_s/dt=K_D(\theta/\rho_b)C(S_{smax}-S_s)$
Langmuir kinetic	$\partial S_s/\partial t=KD(\theta/\rho_b)C(S_{smax}-S_s)-K_{D1}S_s$
Elovich	$\partial S_s/\partial t=A \exp(-BS_s)$
Power	$\partial S_s/\partial t = K_D(\theta/\rho_b)C^n S_s^m$
Mass transfer	$\partial S_s/\partial t=K_D(\theta/\rho_b)(C-C^*)$

^a Where *k*, *A*, *B*, *n*, *m*, *S_s*, *S_{smax}*, *C**, *C_p*, and *ω* are adjustable model parameters.
Source: Modified from Selim and Amacher, 1997.

If the sufficient volume of input solution (concentration=*C*₀) infiltrates in a soil column for a long duration, the excluded water content can be calculated by using Eq. (16.34) (Bond et al., 1982)

$$\theta_{ex} = \theta \left[1 - \frac{C}{C_0} \right] \quad (16.34)$$

The *C* in the soil profile is always lower than *C*₀ when anion exclusion is occurring. The anion exclusion also increases the average velocity of travel of anions in the soil profile. By excluding the anions from the diffuse double layer where water is either moving slowly or is immobile, the rate of transport is greater than given by *q*/*θ*. Bolt (1979) assumed anion exclusion to be evenly distributed over the soil surface of thickness *d_{ex}*.

$$d_{ex} = \frac{Q}{\sqrt{\beta N}} - \delta \quad (16.35)$$

where *β* is a constant (1.06×10¹⁹ mkeq⁻¹ at 25°C), *N* is the total normality of bulk solution (keq m⁻³), *Q* is a factor for ionic composition of bulk solution (m⁻¹), and *δ* a correction term. The specific surface area (*A_r*) can be calculated from exclusion volume and bulk density (*ρ_b*; Mg m⁻³) as follows

$$A_r = \frac{\theta_{ex}}{d_{ex}\rho_b} * 10^{-6} \quad (16.36)$$

16.12 NONEQUILIBRIUM TRANSPORT

The application of Eq. (16.24) or (16.26) to transport through laboratory soil columns or in fields having relatively uniform soils involving nonreactive or weakly reactive solutes was found to be fairly successful (Biggar and Nielsen, 1976; Jaynes, 1991; Ellsworth et al., 1996; Shukla et al., 2003). The BTCs for these tracers are symmetrical and mass recoveries are relatively high (Fig. 16.7). However, for strongly adsorbed chemicals and aggregated soils these equations do not perform very well (van Genuchten and Wierenga, 1976; Nkedi-Kizza et al., 1984).

During solute transport in heterogeneous soils, the assumption of local equilibrium implies instantaneous interchange of mass, large residence time sufficient to make concentration gradients negligible, and high degrees of interactions between macroscopic transport properties and microscopic soil

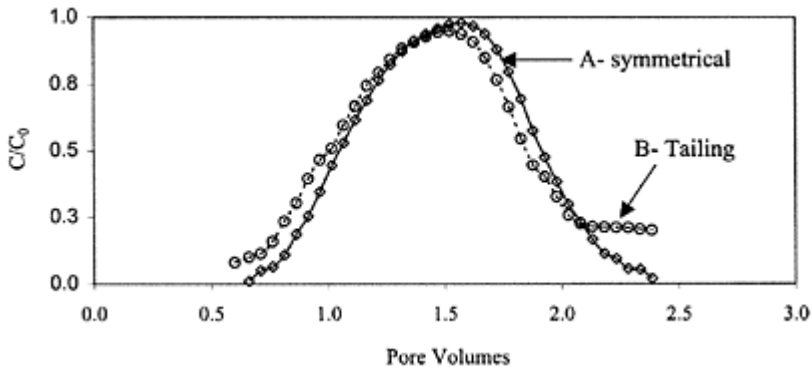


FIGURE 16.7 Schematic of equilibrium and nonequilibrium transport of a tracer through laboratory soil columns, the ETC “A” is symmetrical and mass recoveries are higher than a asymmetrical ETC “B”.

physical properties. Some of the macroscopic transport properties are water flux, apparent dispersion, and moisture content, and microscopic properties are aggregate size, exchange, pore geometry. The microscopic properties impose a rate limiting effect on solute transport through heterogeneous soils and deviations from local equilibrium conditions are observed. The mass recoveries, for these asymmetrical and nonsigmoidal concentration distributions or BTCs, are less and the BTCs have a long tail (Fig. 16.7). Such a deviation is caused by a number of physical and chemical nonequilibrium processes. The physical nonequilibrium is caused by a heterogeneous flow regime and a chemical nonequilibrium by the kinetic adsorption. This paves the way for the examination of diffusion controlled or chemically controlled kinetic rate reactions or both of the form $\partial S/\partial t = f(S, C)$. The following sections will examine briefly the nonequilibrium processes arising out of physical or chemical nonequilibrium.

16.13 TWO-REGION NONEQUILIBRIUM TRANSPORT MODEL

There are several factors responsible for physical nonequilibrium conditions occurring in a soil system during solute transport. Some of them are: (i) heterogeneity of pore size distribution or aggregation; (ii) heterogeneous diffusion into the Neurst film of water surrounding soil particles than soil bulk solution. Physical nonequilibrium is represented by a two-region (dual porosity) type formation. In this case, the medium is assumed to contain two distinct mobile (flowing) and immobile (stagnant) liquid regions. The simplest explanation of a two region mobile and immobile formation is the water inside an aggregated soil. All the intraaggregate water held within an aggregate is immobile and the interaggregate (between aggregates) water is mobile. The water flowing around dry aggregates imbibes them and solute entry inside aggregate is by convection. For moist aggregate, solute entry is governed by diffusion. However, there must be a concentration gradient from outside to the inside of an aggregate, and a first-order process can adequately describe the mass transfer between the two regions. In a two-region model, convective diffusion transport is assumed to take place in the mobile region while transfer of solutes into and out of mobile region is assumed to be diffusion controlled. One-dimensional unsaturated flow of conservative nonsorbing solute in a soil is given as follows (Coats and Smith, 1964):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \quad (16.37)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (16.38)$$

where t is time (T); C_m and C_{im} are the solute concentrations in the mobile and immobile liquid phases (ML^{-3}) with corresponding volumetric moisture contents θ_m and θ_{im} (L^3/L^3) respectively; D_m is apparent diffusion coefficient of mobile liquid phase (L^2T^{-1}); x is the distance from the inflow boundary in the direction of flow (L); v_m is the average mobile pore water velocity in (LT^{-1}); and α is the first order rate coefficient (T^{-1}).

In Eqs. (16.37) and (16.38) as the ratio of mobile water fraction (θ_m) to total moisture content (θ) increases (i.e., θ_m increases), more and more of the wetted pore space is included in the transport, which causes greater and more complete mixing, and the ETC shifts further to the right. At the extreme end, the $\theta_m = \theta$, where the above equation reduces to one-dimensional CDE [Eq. (16.23)]. The parameter α , which has the dimensions of T^{-1} , can vary from 0 to ∞ . A zero value of α indicates no mixing between mobile and immobile water fractions. Therefore, the term on left-hand side of Eq. (16.38) equals zero and Eq. (16.37) reduces to one-dimensional CDE, similar to Eq. (16.23) but with total moisture content of θ_m . When $\alpha = \infty$, the two concentrations mix instantaneously and $C_m = C_{im}$. In this case Eq. (16.37) reduces to Eq. (16.23).

One-dimensional solute transport for an exchanging solute during steady-state flow through a homogeneous porous medium, where the liquid phase is presumed to consist of a mobile and immobile region and includes a Freundlich-type equilibrium adsorption-desorption processes (van Genuchten and Wierenga, 1976) can be described by a two-region model as follows:

$$\begin{aligned} \theta_m \frac{\partial C_m}{\partial t} + f \rho_b \frac{\partial S_{sm}}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f) \rho_b \frac{\partial S_{sim}}{\partial t} \\ = \theta_m D_m \frac{\partial^2 C}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \end{aligned} \quad (16.39)$$

and

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f) \rho_b \frac{\partial S_{sim}}{\partial t} = \alpha (C_m - C_{im}) \quad (16.40)$$

where S_{sm} and S_{sim} are concentration of adsorbed phase in mobile and immobile phase respectively (MM^{-1}); R_m and R_{im} are retardation factors accounting for equilibrium type adsorption processes in mobile and immobile regions, respectively; and parameter/represents the mass fraction of solid phase that is in direct contact with the mobile liquid phase. If the exchange process in both the dynamic (S_{sm}) and stagnant (S_{sim}) region is assumed to be instantaneous, linear and reversible process (van Genuchten, 1981) then,

$$S_{sm} = K_D C_m \text{ and } S_{sim} = K_D C_{im} \quad (16.41)$$

and the total adsorption can be represented by

$$S_s = f S_{sm} + (1-f) S_{sim} \quad (16.42)$$

For equilibrium adsorption, transferring these into Eqs. (16.39) and (16.40) results in following set of equations

$$(\theta_m + \rho_b f k) \frac{\partial C_m}{\partial t} + [\theta_{im} + (1-f) \rho_b k] \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \quad (16.43)$$

$$[\theta_{im} + (1-f) \rho_b K_D] \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (16.44)$$

16.14 TWO-REGION ANION EXCLUSION MODEL

The two-region anion exclusion model divides the total soil-water phase into two compartments, (i) mobile water and (ii) immobile water, and anion exclusion is assumed to take place in the immobile region (van Genuchten, 1981). This assumption is analogous to the assumptions made by Krupp et al. (1972), as anion exclusion takes place in the smaller pores inside the dense aggregate or in the immobile water along the pore wall. An equivalent exclusion distance (d_{ex}) exists near the pore wall where concentration remains zero. Therefore, specific exclusion volume (V_{ex} ; $\text{cm}^3 \text{ water g}^{-1}$ of soil) is related to specific surface area (A_m ; $\text{cm}^2 \text{ g}^{-1}$) and d_{ex} as follows:

$$V_{ex} = d_{ex} A_m \quad (16.45)$$

The θ_{ex} is obtained by multiplying Eq. (45) by soil bulk density (ρ_b)

$$\theta_{ex} = V_{expb} \quad (16.46)$$

The part of liquid phase unaffected by anion exclusion (θ_a) can be calculated as follows:

$$\theta_a = \theta_{im} - \theta_{ex} \quad (16.47)$$

Using Eq. (16.47), the following physical nonequilibrium equation representing the anion exclusion process is obtained (van Genuchten, 1981)

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_a \frac{\partial C_a}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} \quad (16.48)$$

$$\theta_a \frac{\partial C_a}{\partial t} = \alpha (C_m - C_a) \quad (16.49)$$

where C_a is concentration in the part of immobile zone unaffected by exclusion. The model described above assumes anion exclusion taking place inside the immobile water zone. Therefore, convective transport in mobile zone remains unaffected by the exclusion process and C_m never exceeds input concentration C_0 (van Genuchten, 1981).

16.15 TWO-SITE NONEQUILIBRIUM TRANSPORT MODEL

Considering that the solid phase of soil is made up of various constituents (i.e., soil minerals, organic matter, aluminum, and iron oxides), and chemical react with these different constituents at different rates and intensities. Selim et al. (1976) and Cameron and Klute (1997) proposed a two-site chemical nonequilibrium model where adsorption term consists of two components, equilibrium adsorption, and first-order kinetics. The sorption or exchange sites in this model are assumed to have instantaneous adsorption (type-1 sites) and time-dependent kinetic adsorption (type-2 sites). At equilibrium, adsorption on both types of sorption sites is described by the following linear equations:

$$S_{s1} = K_{De} C = F K_D C \quad (16.50)$$

$$S_{s2} = K_{Dk} C = (1-F) K_D C \quad (16.51)$$

where subscript “e” refers to type 1 or equilibrium site and subscript “k” refers to type 2 or kinetic sites, respectively, and F is the fraction of all sites occupied by type 1 sorption sites. Total adsorption at equilibrium is

$$S_s = S_{se} + S_{sk} \quad (16.52)$$

Because type 1 sites are always at equilibrium therefore,

$$\frac{\partial S_{se}}{\partial t} = FK_D \frac{\partial C}{\partial t} \quad (16.53)$$

The adsorption rate for type 2 kinetic nonequilibrium sites can be given by a linear and reversible first order equation of following form

$$\frac{\partial S_{sk}}{\partial t} = \alpha[(1 - F)K_D C - S_{sk}] \quad (16.54)$$

where α is the first order rate coefficient. Combining above equations with Eq. (16.14) lead to following formulation (van Genuchten, 1981; Nkedi-Kizza et al., 1984):

$$\left(1 + \frac{F\rho_b K_D}{\theta}\right) \frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S_{sk}}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (16.55)$$

$$\frac{\partial S_{sk}}{\partial t} = \alpha[(1 - F)K_D C - S_{sk}] \quad (16.56)$$

16.16 INITIAL AND BOUNDARY CONDITIONS FOR STEP INPUT EXPERIMENTS

The analytical solutions of Eqs. (16.23), (16.24), (16.25), (16.43), (16.44), (16.48), (16.49), (16.55), and (16.56) are available for a large number of initial and boundary conditions for both finite and semi-infinite systems for both step and pulse type solute application (van Genuchten 1981, van Genuchten and Alves, 1982). This section briefly describes some of the initial and boundary conditions required for solving solute transport equations. The most common initial condition for any soil is:

$$C(x, 0) = C_i \quad (16.57)$$

At the upper boundary of the soil surface or (or inflow into the soil column; i.e. at $x=0$), two different boundary conditions can be considered. The first type or constant concentration boundary condition is of the form as follows:

$$C(0, t) = C_0 \quad (16.58)$$

For column displacement experiments, where chemical is applied at a constant rate, the boundary condition (16.58) leads to mass balance errors, which become quite significant for large values of (D/v) (van Genuchten, 1981, Parker and van Genuchten, 1984). The other boundary condition is a third type, or constant flux type, that leads to the conservation of mass inside the soil column provided dispersion outside the soil can be ignored is given as follows:

$$\left[-D \frac{\partial C}{\partial x} + vC \right]_{x=0} = vC_0 \quad (16.59)$$

A third type inlet condition is usually preferred over first type inlet condition (van Genuchten and Parker, 1984, Toride et al., 1993). In order to describe the outlet conditions, it is assumed that the concentration is macroscopically continuous at the outlet and no dispersion occurs outside the soil. Parker and van Genuchten, (1984) suggested that by assuming that the upstream solute concentrations are not affected by the outlet boundary, solutions for an infinite outlet condition can be applied to the finite region. The outlet condition for a semi infinite profile ($0 \leq x < \infty$) and a finite system of length L can be specified in terms of zero concentration gradient as below

$$\left(\frac{\partial C}{\partial x} \right) (\infty, t) = 0 \quad (16.60)$$

$$\left(\frac{\partial C}{\partial x} \right) (L, t) = 0 \quad (16.61)$$

The boundary condition [Eq. (16.60)] assumes a semi-infinite soil column and is commonly used. When effluent curves from finite columns are calculated using analytical solutions based on boundary condition [Eq. (16.60)], some errors may be introduced. Therefore, zero concentration gradient at the upper end of the column as specified by Eq. (16.61) is frequently used for column displacement studies. However, there is no evidence available to prove that the boundary condition Eq. (16.61) leads to a better description of physical processes at and around $x=L$. On the other hand, the boundary condition [Eq. (16.59)] gives a discontinuous distribution at the inlet, which is against the requirement of a continuous distribution at $x=L$ (van Genuchten, 1981).

16.17 DIMENSIONAL INITIAL AND BOUNDARY CONDITIONS FOR PULSE APPLICATION

Assuming that the concentrations are continuous across the inlet boundary and that input solution is well mixed, a first type boundary condition across the inlet boundary for a pulse type injection can be specified as (van Genuchten, 1981):

$$\begin{aligned} C(0, t) &= C_0 \quad 0 < t < t_0 \\ C(0, t) &= 0 \quad t > t_0 \end{aligned} \quad (16.62)$$

A third type boundary condition for the pulse input for a well mixed input solution can be specified as

$$\begin{aligned} [-D(\partial C/\partial x) + vC]_{x=0} &= vC_0 \quad 0 < t \leq t_0 \\ [-D(\partial C/\partial x) + vC]_{x=0} &= 0 \quad t > t_0 \end{aligned} \quad (16.63)$$

The two-site model [Eqs. (16.55) and (16.56)] can be solved for the boundary and initial conditions given by Eqs. 16.57 to 16.61. One additional initial condition for the solution is

$$S_{sk}(x, 0) = (1-F)K_D C_i \quad (16.64)$$

The initial condition and the boundary conditions at exit remain the same as described by Eqs. (16.52), (16.55), and (16.56). The boundary condition at inlet, Eq. (16.57), becomes inappropriate when the input solution is not well mixed. Other arguments against the applicability of Eq. (16.57) can be that the plane considered as a macroscopic boundary has no physical relevance at the microscopic level, as irregularity in pore structure and morphology become manifest at this level. Also the medium properties vary continuously over a finite transition zone of $l/2$, where l is the representative elementary volume (REV) of the porous medium (Parker and van Genuchten, 1984).

16.18 THE COMBINED NONDIMENSIONAL TRANSPORT EQUATIONS

Nonequilibrium transport Eqs. (16.31), (16.32), (16.36), (16.37), (16.43), and (16.44) are mathematically equivalent and transferring nondimensional quantities listed in Table 16.4 reduces them to the following combined nondimensional equations (van Genuchten, 1981; Nkedi-Kizza, 1984)

$$\beta R \frac{\partial C_1}{\partial T} + (1 - \beta) R \frac{\partial C_2}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} \quad (16.65)$$

$$(1 - \beta) R \frac{\partial C_2}{\partial T} = \omega (C_1 - C_2) \quad (16.66)$$

where β is partition coefficient, ω is nondimensional mass transfer parameter and P is pecllet number. Initial and boundary conditions for a step type input are

$$C_1(x, 0) = C_2(x, 0) = 0 \quad (16.67)$$

$$-\frac{1}{P} \frac{\partial C_1}{\partial x} + C_1|_{x=0} = 1 \quad (16.68)$$

$$\frac{\partial C_1}{\partial x}(\infty, T) = \frac{\partial C_2}{\partial x}(\infty, T) = 0 \quad (16.69)$$

For $\beta=1$, Eqs. (16.65) and (16.66) reduce to the nondimensional CDE. Some of the analytical solutions of Eqs. (16.17), (16.65), and (16.66) are given in Table 16.5.

16.19 ESTIMATION OF SOLUTE TRANSPORT PARAMETERS

The equilibrium solute transport equation [refer to Eq. (16.17)] has two parameters: (i) the apparent diffusion coefficient (D) or P (vL/D) and (ii) the retardation factor (R).

TABLE 16.4 Nondimensional Variables
Introduced in the Solute Transport Equations

The nondimensional variables

FOR ALL THE EQUATIONS

$$T = \frac{vt}{L} \quad Z = \frac{x}{L} \quad P = \frac{vL}{D} \quad R = 1 + \frac{\rho K_D}{\theta} \quad C_1 = \frac{C - C_i}{C_0 - C_i}$$

FOR TWO REGION EQUATION

$$R_m = 1 + \frac{F\rho K_D}{\theta_m} \quad \beta = \frac{\theta + F\rho K_D}{\theta + \rho K_D} = \frac{R_m}{R} \quad \omega = \frac{\alpha_2(1 - \beta)RL}{v} \quad C_2 = \frac{S_{s2} - (1 - F)K_D C_i}{(1 - F)K_D(C_0 - C_i)}$$

FOR TWO REGION EQUATION

$$C_1 = C_m/C_0 \quad C_2 = C_m/C_0 \quad P = \frac{v_m L}{D_m} \quad \phi_m = \frac{\theta_m}{\theta} \quad \omega = \frac{\alpha L}{q}$$

$$R_m = 1 + \frac{f\rho K_D}{\theta_m} \quad R_{im} = 1 + \frac{(1 - f)\rho K_D}{\theta_{im}} \quad \beta = \frac{\theta_m + f\rho_b K_D}{\theta + \rho_b K_D} = \frac{\phi_m R_m}{R}$$

$$C_1 = \frac{C_m - C_i}{C_0 - C_i} \quad C_2 = \frac{C_{im} - C_i}{C_0 - C_i} \quad T = \frac{v_m \phi_m t}{L} \quad q = \theta_m v_m$$

Source: Modified from van Genuchten, 1981.

TABLE 16.5 Analytical Solutions of Equilibrium CDE and Nonequilibrium (NE) Transport Equations

	Concentration-type boundary conditions	Flux-type boundary conditions
Concentration	$C_1(0, T) = 1$ $\frac{\partial C_1(\infty, T)}{\partial Z} = 0$	$\left(-\frac{1}{P} \frac{\partial C_1(Z, T)}{\partial Z} + C_1(Z, T) \right) \Big _{z=0} = 1$ $\frac{\partial C_1(\infty, T)}{\partial Z} = 0$
	$C_e = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} \cdot (R - T) \right]$ $+ \frac{1}{2} \exp(P) \cdot \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} \cdot (R + T) \right]$	$C_e = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} \cdot (R - T) \right]$ $+ \left(\frac{PT}{\pi R} \right)^{1/2} \cdot \exp \left[-\frac{P}{4RT} \cdot (R - T)^2 \right]$ $- \frac{1}{2} \cdot \left(1 + P + \frac{PT}{R} \right) \cdot \exp(P)$ $\cdot \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} \cdot (R + T) \right]$

$$\begin{aligned}
 G(\tau) &= \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4\beta R\tau} \right)^{1/2} \cdot (\beta R - \tau) \right] & G(\tau) &= \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4\beta R\tau} \right)^{1/2} \cdot (\beta R - \tau) \right] \\
 &+ \frac{1}{2} \exp(P) \cdot \operatorname{erfc} \left[\left(\frac{P}{4\beta R\tau} \right)^{1/2} \cdot (\beta R - \tau) \right] & &+ \left(\frac{P\tau}{\pi\beta R} \right)^{1/2} \cdot \exp \left[-\frac{P}{4\beta R\tau} \cdot (\beta R + \tau)^2 \right] \\
 & & &- \frac{1}{2} \cdot \left(1 + P + \frac{P\tau}{\beta R} \right) \\
 & & &\cdot \exp(P) \cdot \operatorname{erfc} \left[\left(\frac{P}{4\beta R\tau} \right)^{1/2} \cdot (\beta R + \tau) \right] \\
 F(\tau) &= \frac{\beta}{\tau} \left(\frac{PR}{4\pi\beta\tau} \right)^{1/2} \cdot \exp \left[-\frac{P}{4\beta R\tau} \cdot (\beta R - \tau)^2 \right] & F(\tau) &= \left(\frac{P}{\pi\beta R\tau} \right)^{1/2} \cdot \exp \left[-\frac{P}{4\beta R\tau} \cdot (\beta R - \tau)^2 \right] \\
 & & &- \frac{P}{2\beta R} \cdot \exp(P) \cdot \operatorname{erfc} \left[\left(\frac{P}{4\beta R\tau} \right)^{1/2} \cdot (\beta R + \tau) \right]
 \end{aligned}$$

Source: Modified from van Genuchten, 1981.

16.19.1 Retardation Factor (R)

From Measured Breakthrough Curve

The retardation factor (R) can be estimated by locating the number of pore volumes ($T=R$) at which the relative concentration of the measured ETC is 0.5. For the measured chloride ETC in Fig. 16.8, the value of T at C/C_0 of 0.5 is 1.2. Therefore, the value of R is also 1.2. Both pore volumes (T) and retardation factor (R) are dimensionless.

From Batch Experiment

The batch experiments for solute adsorption are performed by mixing air-dried soil and solution (1:1). At least six different initial solution concentrations, which are within the experimental range, are usually selected. Generally three to four replications for each concentration are made. The mixture is stirred, and after equilibrating for 24 hours, is centrifuged and the concentration of the extracted solution is measured. The difference between the initial solution concentration and that in the supernatant (centrifuge) is assumed to be the result of adsorption. A graph is plotted between the solution concentration and the adsorbed concentration (Fig. 16.6) and the slope of the line gives the value of distribution coefficient (K_D). The R can be calculated from Eq. (16.18) for known values of bulk density and water content of soil in the experiment.

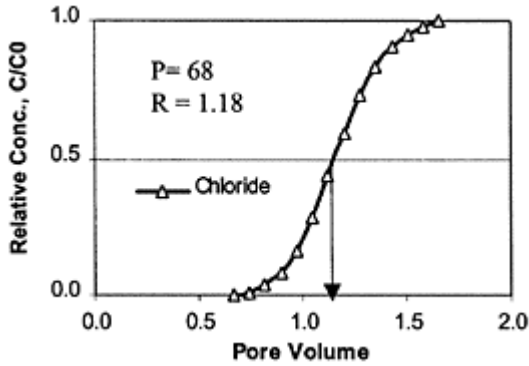


FIGURE 16.8 The estimation of retardation coefficient from a measured ETC ($R=T=1.2$) where T is pore volumes. (Redrawn from Shukla and Kammerer, 1998.)

By Fitting Flow Velocity

The pore water velocity can be used as a fitting parameter in the trial and error method while keeping R a constant and equal to 1. Therefore, fitted velocity will effectively be a v/R value. The slope of the plot between fitted and measured pore water velocity gives an effective R -value.

From Travel Time Analysis

Time moment analysis provides a model independent tool for characterizing the solute BTCs. The first temporal moment provides the mean break-through time, the second central temporal moment (i.e., the variance) describes the solute spreading, and the third (skewness) describes the degree of asymmetry of the BTCs (Valocchi, 1985). These numerical estimates can be compared to the CDE theoretical travel time moments to provide estimates of the CDE model parameters, in contrast to least-squares fitting of the analytical solution to Eqs. (16.23) and (16.24). For a finite pulse, the expected or theoretical mean travel time to depth L is:

$$\frac{RL}{v} + \frac{t_0}{2} \quad (16.70)$$

and the theoretical travel time variance is

$$\frac{2DR^2L}{v^3} + \frac{(t_0)^2}{12} \quad (16.71)$$

where R is retardation factor, D is apparent dispersion coefficient (cm^2h^{-1}), v is pore water velocity (cmh^{-1}), t_0 is the duration of pulse (h), and L is the displacement length (cm). For the step input experiments, a smooth cubic spline to each BTC can be fitted, and then the derivatives can be computed with respect to time. The center of mass of an inert solute pulse under steady flow at a given average measured pore water velocity (v) is model independent and moves at the same rate as the average v . However, different process models often result in quite different rates of spreading or dispersion but these do not affect the mean travel time (Valocchi, 1985). The slope of the best-fit curve between observed and theoretical travel times provides the effective R-value with intercept equal to zero. For details on travel moment analysis readers are advised to refer Jury and Roth (1990).

16.19.2 Apparent Dispersion Coefficient

The apparent dispersion coefficient (D) can be estimated by the following methods.

Trial and Error Method

The parameters D (or P) can be estimated by comparing the experimentally measured ETC with a series of calculated distributions. The distributions can be calculated for a known value of R ($=T$) by selecting several values of P (1, 2, 4, 5, 10, 20, 50, 100, 300, etc.). The value of P , which provides the best fit between the experimental and calculated BTC is chosen, and D is calculated from the known values of displacement length and pore water velocity ($D=vLP$).

From Slope of an Effluent Curve

The apparent diffusion coefficient can be approximated by an experimental BTC from the following equation (Kirkham and Powers, 1972)

$$D = \frac{vL}{4\pi m^2} \quad (16.72)$$

where m is the slope of BTC at one pore volume, i.e.,

$$m = \left. \frac{\partial(C/C_0)}{\partial p} \right|_{p=1} \quad (16.73)$$

Log Normal Plot of Effluent Curve

In this method the inverse complimentary error function of relative concentration (see Table 16.5) from the experimentally determined BTC is plotted against log of pore volumes (T). The value of P is estimated from the slope (m) of above straight line ($P=4*m^2-b$, where b is a correction factor) (van Genuchten and Wierenga, 1986).

Least Square Analysis

The trial and error method is expanded into a more rigorous approach by continuously adjusting the values of P and R until the sum of the

TABLE 16.6 Merits and Demerits of Approximate Methods of Solute Transport Parameter Estimation

Method	Merits	Demerits
Trial and error	Provide first estimates of P and R quickly	Method is not necessarily reproducible
From slope of ETC	Method is simple and based upon analytical solution. For conservative solutes works reasonably well.	Method is not suitable for small values of P and for nonconservative solutes
Log normal plot	Results are more accurate than the above two methods	Straight line is not generally obtained. Method is not suitable for aggregated or structured soils
Least square analysis	Results are the most accurate among all the methods described above. Computer programs are available and easy to use. Number of fitting parameters can be varied according to the need	User judgment is necessary for reporting fitted values of parameters

squared deviations between measured and fitted concentrations are minimized in a least square sense (van Genuchten and Wierenga, 1986). The merits and demerits of all the methods described above are presented in Table 16.6.

16.19.3 Parameters of TRM

The physical nonequilibrium model or two-region model (TRM) requires specification of four dimensionless parameters P (v_m, L, D), R (ρ_b, K_D, θ), β ($\phi, \theta_m, \theta_{im}, f$) and ω (α, L, θ_m, v_m) [refer Eqs. (16.65) and (16.66)]. The parameters of TRM can be estimated by a number of ways:

Least Square Fitting

The first option is to use a trial-and-error method and fit all the four-nondimensional parameters to the measured breakthrough curve, also known as “inverse modeling technique,” by minimizing the sum of squares between measured and fitted breakthrough curves using a nonlinear least square method. The second option is to determine R from the batch experiment and obtain the remaining three-nondimensional parameters by least square fit. It should be remembered while using the least square method that for P values >5 , the least square fitting method is appropriate, however for $P < 5$, the problems associated with conservation of mass become important and trial and error method remains no longer appropriate. The lower P values also suggest extremely broad range in pore water velocity distributions in mobile water region, which renders division of flow

domain into two flow regions inadequate. A possible solution is to divide flow domain in more compartments (Morisawa et al., 1986) or consider pore water velocity to be a continuous function (White et al., 1986).

Mobile (θ_m) and Immobile (θ_{im}) Water Contents

The total moisture content (θ) of the soil is the sum of the mobile (θ_m) and immobile (θ_{im}) moisture contents. The mobile and immobile water can be estimated in a number of ways: (i) all the water held at field capacity (24 h after the infiltration test or at suction of 330 kPa) can be considered as immobile water. Therefore, mobile water (θ_m) can be obtained by subtraction the θ_{im} from total water content of soil (θ) as follows:

$$\theta_m = \theta - \theta_{im} \quad (16.74)$$

(ii) The total concentration in soil after infiltration test is given by a mass balance equation as follows:

$$\theta C = \theta_m C_m + \theta_{im} C_{im} \quad (16.75)$$

A conservative tracer such as bromide (Br) or chloride (Cl) of known initial concentration (C_0) used as a solute is infiltrated into the soil. After the steady state infiltration with tracer solution is achieved, the concentration of the solute extracted from soil sample (C) below the infiltration can be measured. If all the soil moisture is mobile than C equals C_0 . If immobile moisture is present $C < C_0$ and θ_{im} can be obtained as follows (Clothier, et al., 1992):

$$\theta_m = \theta \frac{C}{C_m} = \theta \frac{C}{C_0} \quad (16.76)$$

alternately

$$\theta_{im} = \theta \left(1 - \frac{C}{C_0} \right) \quad (16.77)$$

The above equation assumes that transfer coefficient (α) in Eq. (16.56) is small and very little solute diffuses into the immobile region.

The θ_{im} and α

The θ_{im} and α can also be estimated simultaneously by applying a sequence of nonconservative nonreactive tracers for varying periods of time (Jaynes et al., 1995).

Eq. (16.37) after separating the variables can be written as follows:

$$\ln \left(1 - \frac{C}{C_0} \right) = \frac{-\alpha}{\theta_{im}} t + \ln \left(\frac{\theta_{im}}{\theta} \right) \quad (16.78)$$

where t is defined as the application time and varies for different tracers, Plotting the $\ln(1-C/C_0)$ versus t , for all the tracers, gives straight lines with negative slopes (Fig. 16.9). The intercept at $t=0$ gives natural log of the

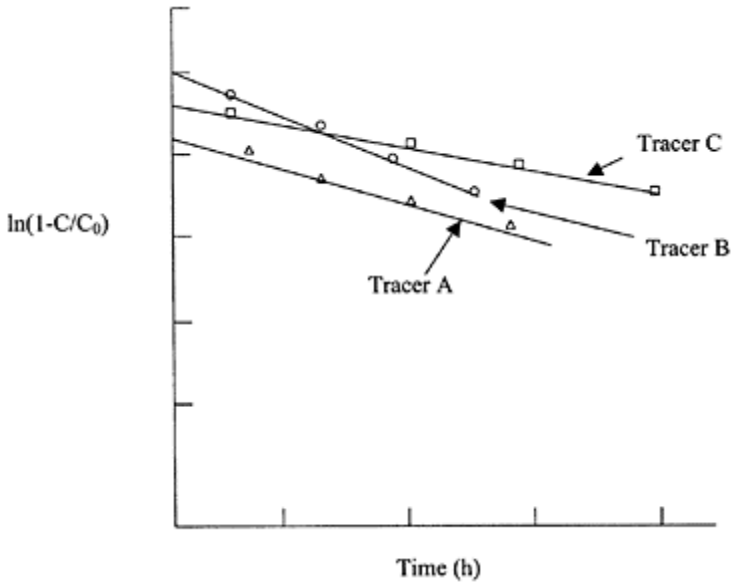


FIGURE 16.9 A schematic of normalized concentration of tracers and the time of application.

ratio of immobile water and total moisture content [the second term on right-hand side of Eq. (16.78)]. For a known θ , θ_{im} can be estimated by multiplying the intercept with θ and making appropriate \ln transformations. The first term of Eq. (16.78) gives the slope and for a known θ_{im} , α can be easily calculated. The tracer front will reach a given sampling depth (d) slightly earlier than specified by t . Therefore, t in Eq. (16.78) can be replaced by " $t-d/v_m$ " and Eq. (16.77) becomes (Jaynes and Horton, 1998):

$$\ln\left(1 - \frac{C}{C_0}\right) = \frac{d\alpha}{\theta_{im}v_m} + \ln\left(\frac{\theta_{im}}{\theta}\right) - \frac{\alpha}{\theta_{im}}t \quad (16.79)$$

The θ_{im} and α can again be measured by plotting the $\ln(1 - C/C_0)$ versus t . It should clearly understood that the assumption $C_m=C_0$ associated with Eqs. (16.76) to (16.79) may not be correct for $a>0$.

By Making Approximations

The partition coefficient “ β ” can be obtained by using the inverse modeling technique from a measured breakthrough curve. The β , f and ϕ_m are related by the following equation, which shows that from a known value of β the f and ϕ_m cannot be calculated directly:

$$\phi_m = [R\beta - f(R - 1)] \quad (16.80)$$

If R is close to 1 then

$$\phi_m = \beta \quad (16.81)$$

For $R \neq 1$, the mobile water fraction (ϕ_m), which is the ratio of θ_m and θ , can be calculated from known field capacity water content and Eq. (16.74). A better option for obtaining the values of ϕ_m or β is to make some assumptions on f , which is defined as the fraction of sorption sites in mobile region. When soil is saturated and distribution of sorption sites is independent of the location in soil-water regions (Seyfried and Rao, 1987)

$$f = \phi_m = \beta \quad (16.82)$$

However, the assumption that more sites for adsorption are available in the immobile region is more appropriate (Nkedi-Kizza et al., 1982). This assumption is appropriate because the pores in immobile regions are smaller and have higher exposed surface area than in mobile region. Therefore, f can be assumed to vary from 0 to $\phi_m/2$ (Seyfried and Rao, 1987).

Aggregate Geometry Models

The nondimensional mass transfer parameter (ω) is not directly related to any specific soil characteristic or property and is difficult to determine. The α is a function of time of diffusion, sphere radius (particles constituting the porous medium), molecular diffusion coefficient, intraaggregate water content (θ_{im}), macroporosity (fraction of total porosity); therefore, apart from Eqs. (16.78) and (16.79), the α can be calculated for the known or assumed geometry of aggregates. For spherical aggregates α can be calculated as follows (Rao et al., 1980).

$$\alpha = \frac{D_e(1-f)\theta}{r^{20}} \alpha^* \quad (16.83)$$

where D_e is the effective diffusion coefficient, r is the radius of sphere, and α^* is time dependent variable. The α values of cubic aggregates can be obtained by replacing “ a ” with an equivalent spherical radius “ $r=0.6203l$ ”, where l is the length of the side of the cube (Rao et al., 1982). Another widely used formula for the estimation of α based on soil geometry is (van Genuchten, 1985; van Genuchten and Dalton, 1986):

$$\alpha = \frac{nD_e(1-f)\theta}{a_e^2} \quad (16.84)$$

where n is a geometry factor, and a_e is an average effective diffusion length. If a soil matrix, with overall conductivity of K_e , can be divided into a two-flow domain physical nonequilibrium model. The water contents of these flow regions are θ_A and θ_B for velocities v_A and v_B , respectively. For steady flow condition the α can be estimated as follows (Skopp et al., 1981):

$$\alpha = \frac{2K_e\theta_A(v_A - v_B)^2}{gdr_p\pi} \quad (16.85)$$

where d is the aggregate size (cm), r_p is the interaggregate pore size (cm), and g is acceleration due to gravity (cmh^{-2}). It should be remembered here that α values estimated using aggregate geometry models does not necessarily fit the measured breakthrough curves very well. The α values depend on the experimental conditions (Ma and Selim, 1998). In general α values increase with flow velocity probably as a result of turbulent mixing at high velocities (van Genuchten and Wierenga, 1977). However, α values decrease if greater pore connectivity exists in the flow domain (Skopp and Gardner, 1992).

16.20 Land Use Effects on Flow and Transport

The flow and transport properties of soils often vary with time due to the influence of land use and soil management practices. The soil remains mostly undisturbed under no-till, which enhances the organic matter accumulation at the soil surface and development of macropores (cracks between aggregates and pores). The macropore channels in no-till system increase the leaching of nutrients and pesticides by bypassing the water-filled micropores unless the sources are located within the soil micropores. These cracks increase the hydraulic conductivity of soil and decrease reactivity of dissolved chemicals due to the low pore surface area and short residence time. The increase in organic matter increases the reactivity of chemicals in the soil matrix and the soils start behaving as a multireaction, multiregion soil. It is important to know this shift in flow and transport processes due to macropores as failure to take these into account can lead to erroneous conclusions. For an example: In a macroporous soil system, a zero-tension lysimeter was installed at a 90-cm depth, which captured 50% of the applied pesticide leached out of root zone system via macropore channels. The analysis of soil samples at different depth increments showed very little traces of pesticides. Therefore, without having the knowledge of preferential flow of pesticides, an inaccurate conclusion that pesticides had limited mobility due to high degradation rates can be drawn. Similarly, an increase in organic matter provides kinetic adsorption sites for some solutes, which would lead to inaccurate results if lumped into instantaneous equilibrium adsorption terms (Wilson et al., 2000).

Example 16.1

Concentration of a solute is 30 mg/g of soil and bulk density is 1.35 Mg/m³. Assuming steady flow conditions, solute free soil profile, and solute diffusion coefficient $3 \times 10^{-10} \text{ m}^2/\text{s}$, calculate flux density at a vertical distance of 0.1 m and amount of solute in 1 ha that diffuses across this boundary in 2 months. (Hint: Use Fick's first law.)

Solution

Solute concentration = $\rho_b \cdot C_a = 30 \cdot 1.35 = 40.5 \text{ M/gm}^3$ or $4.05 \times 10^7 \text{ mg/m}^3$

Concentration gradient at 0.1 m below soil surface

$$\delta C / \delta z = \Delta C / \Delta z = (0 - 4.05 \times 10^7) / (0 - 0.1) = 4.05 \times 10^8 \text{ mg/m}^4$$

The flux density of solute is obtained by using equation 7

$$J = -(3 \times 10^{-10}) \cdot (4.05 \times 10^8) = -0.122 \text{ mg m}^{-2} \text{ s}^{-1}$$

The negative sign implies that solute is moving downward. The total quantity of solute moved below 0.1 m in one month (Q) can be calculated as

$$Q = 0.122 \cdot 10000 \cdot 30 \cdot 24 \cdot 3600 = 3.16 \times 10^9 \text{ mgha}^{-1}$$

Example 16.2

Nitrate-N was applied in a field at volumetric moisture content of 0.35. If soil water flux density was 0.05 cm d^{-1} and soil solution concentration of $\text{NO}_3\text{-N}$ was 4 mg L^{-1} , calculate the pore water velocity and amount of $\text{NO}_3\text{-N}$ leached per unit area by convective flow below the root zone in 2 days.

Solution

Pore water velocity = $v = q / \theta = 0.05 / 0.35 = 0.143 \text{ cm/d}$

The flux density for convective transport (J_m) can be calculated from equation 6.

$$J_m = qC = 0.05 \cdot 4 \cdot 1000 / 1000 = 2.0 \text{ mg/m}^2 \text{ d}$$

Therefore, amount of $\text{NO}_3\text{-N}$ (Q) leached through root zone in 2 days

$$Q = J_m \cdot A \cdot t = 2 \cdot 1 \cdot 2 = 4 \text{ mg}$$

Example 16.3

Assuming steady condition and piston flow through a soil column at moisture content of $0.35 \text{ cm}^3 \text{ cm}^{-3}$, calculate the total time required to transport chloride from the bottom of the root zone to groundwater at 50 m below when average daily drainage rate is 0.25 m/d .

Solution

Total depth of water in the vadose zone = $0.35 \times 50 = 17.5$ m The breakthrough time (total time required) to transport all the chloride to groundwater = $17.5 / 0.25 = 70$ d Alternately, pore water velocity of chloride ($v = q / \theta$) = $0.25 / 0.35 = 0.71$ m/d Breakthrough time ($t^* = L / v$) = $50 / 0.71 = 70$ d

Example 16.4

Using the information in Example 3, calculate the velocity and breakthrough time for chloride if bulk density of soil was 1.4 Mg/m^3 and the slope of equilibrium isotherm was $0.06 \text{ m}^3 \text{ Mg}^{-1}$.

Solution

The retardation factor (R) = $1 + k^* \rho_b / \theta = 1 + 0.06 \times 1.4 / 0.35 = 1.24$ Average chloride velocity = $0.25 / (0.35 \times 1.24) = 0.58$ m/d The breakthrough time = $50 / 0.58 = 86$ days

PROBLEMS

1. In a repacked loam soil column with total porosity (ϕ) of 0.5, the measured dispersivity (λ) was 1.2. Assuming that diffusion coefficient of solute in water (D_0) is $1 \text{ cm}^2 \text{ day}^{-1}$, calculate remaining parameters given in the table below.

Note: Tortuosity factor (ξ) is given as $\xi = \theta^{10/3} / \phi^2$ (known as the Millington– Quirk formula, 1961). Effective-dispersion diffusion coefficient (D) is given by $D_e = D_h + D_m$.

$q \text{ (cm.d}^{-1}\text{)}$	θ	$v \text{ (cm.d}^{-1}\text{)}$	ξ	D_h	D_m	D
0.2	0.25					
1	0.3					
2	0.35					
5	0.4					

2. Assume that average volumetric water content (θ) of soil is 0.2; and bulk density (ρ_b) is 1.5 g cm^{-3} . The average annual drainage rate (dr) is 0.5 myr^{-1} . If a pesticide, $Kd = 2 \text{ cm}^2 \text{ g}^{-1}$, is applied to this soil, calculate how long (breakthrough time) it will take to move the pesticide to the groundwater at (L) 12 m depth.

3. Chloride solution was applied as a step input to a 10 cm long soil column initially saturated with water. The flux density of chloride (q) was 0.5 cm h^{-1} , and average water content of column was $0.45 \text{ cm}^3 \text{ cm}^{-3}$. The chloride ETC can be plotted on an Excel spreadsheet with X-axis as pore volumes (p) and relative chloride concentration (C/C_0). The pore volumes are 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 and corresponding C/C_0 are 0.01, 0.06, 0.15, 0.3, 0.54, 0.8, 0.96, and 0.99 respectively. Calculate the apparent diffusion coefficient (D) and retardation coefficient (R).

REFERENCES

- Bear J. (1972). Dynamics of fluid in porous media. Elsevier Science, New York.
- Bear J. and Y.Bachmat (1967). A generalized theory on hydrodynamic dispersion in porous media. Symp. Artificial Recharge Management Aquifers, Haifa, Int. Assoc. Sci. Hydrol., 72:7–36.
- Biggar J.W. and D.R.Nielsen (1967). Miscible displacement and leaching phenomenon. *Agronomy* 11:254–274.
- Bolt G.H. (1979) (ed.). Soil chemistry. B: Physio-chemical models. Elsevier Scientific Pub. Co., New York.
- Bond W.J., B.N.Gardiner, and D.E.Smiles (1982). Constant flux adsorption of a tritiated calcium chloride solution by a clay soil with anion exclusion. *Soil Sci. Soc. Am. J.* 46:1133–1137.
- Bresler E. (1973). Anion exclusion and coupling effects in a nonsteady transport through unsaturated soils: I. Theory. *Soil Sci. Soc. Am. Proc.* 37:663–669.
- Butters G.L., W.A.Jury, and F.F. Ernst (1989). Field scale transport of bromide in an unsaturated soil. 1. Experimental methodology and results. *Water Resour. Res.* 25:1575–1581.
- Cameron D.R. and A.Klute (1977). Convective–Dispersive solute transport with a combined equilibrium and kinetic adsorption model. *WRR*, 13(1): 183–188.
- Clothier B.E., M.B.Kirkham, and J.E.Mclean (1992). In situ measurements of the effective transport volumes for solute moving through soil. *Soil Sci. Soc. Am. J.* 56:733–736.
- Coats K.H. and B.D.Smith (1964). Dead end pore volume and dispersion in porous media. *SPE J.* 4:73–84.
- De Josselin De Jong G. (1958). Longitudinal and transverse diffusion in granular deposits. *Trans. Amer. Geophys. Union* 59:67.
- Ellsworth T.R., P.J.Shouse, T.H.Skaggs, J.A.Jobes, and J.Fargerlund (1996). Solute transport in unsaturated soil: experimental design, parameter estimation, and model discrimination. *Soil Sci. Soc. Am. J.* 60:397–407.
- Fleming J.B. and G.L. Butters (1995). Bromide transport detection in tilled and nontilled soil: solute samplers vs. soil cores. *Soil Sci. Soc. Am. J.* 59: 1207–1216.
- Flury M., W.A.Jury, and E.J.Kladivko (1998). Field scale solute transport in vadose zone: Experimental observations and interpretation. In: H.M. Selim and L. Ma (eds.), *Physical Nonequilibrium in Soils*. Ann Arbor Press, Michigan, p 349–365.
- Fried J.J. and M.A.Combarous (1971). Dispersion in porous media. *Ad. Hydroci.* 7:169–282.
- Greenkorn R.A. (1983). Flow phenomena in porous media. Marcel Dekker Inc., New York and Basel, p 190.
- Hamlen C.J. and R.G.Kachanowski (1992). Field solute transport across a soil horizon boundary. *Soil Sci. Soc. Am. J.* 56:1716–1720.
- James R.V. and J.Rubin (1986). Transport of chloride ion in a water unsaturated soil exhibiting anion exclusion. *Soil Sci. Soc. Am. J.* 50:1142–1149.
- Jaynes D.B. (1991). Field study of bromacil transport under continuous flood irrigation. *Soil Sci. Soc. Am. J.* 55:658–664.
- Jaynes D.B., S.D.Logsdon, and R.Horton (1995). Field method for measuring mobile/immobile water content and solute transfer rate coefficient. *Soil Sci. Soc. Am. J.* 59:352–356.
- Jury A.W. and K.Roth (1990). Transfer functions and solute movement through soil. Birkhaeuser Verlag, Basel, Germany.
- Jury A.W., W.R.Gardner, and W.H.Gardner (1991). *Soil physics*, 5th Edition, John Wiley, New York.
- Torelli L. and A.E. Scheidegger (1972). Threedimensional branching type models of flow through porous media. *J. Hydro.* 15:23.
- Kirkham D. and W.L.Powers (1972). *Advanced soil physics*. Wiley Interscience, John Wiley & Sons, Inc., New York.
- Krupp H.K. and D.E.Elrick (1968). Miscible displacement in an unsaturated glass bead medium. *Water Resour. Res.* 4:809–815.

- Krupp H.K., J.W.Biggar, and D.R.Nielsen (1972). Relative flow rates of salt and water in soil. *Soil Sci. Soc. Am. Proc.* 36:412–417.
- Kutilek M. and D.R.Nielsen (1994). *Soil Hydrology*. Catena Verlag, CremlingenDestedt, Germany.
- Lapidus L. and N.R.Amundson (1952). Mathematics of adsorption in beds. *J. Phys. Chem.* 56:584.
- Ma L. and H.M.Selim (1998). Physical nonequilibrium in soils: modeling and application. In: H.M.Selim and L.Ma (eds.), *Physical Nonequilibrium in Soils*. Ann Arbor Press, Michigan, p 83–115.
- Morisawa S., M.Horiuchi, T.Yamaoka, and Inoue Y. (1986). Evaluation of solute transport in unsaturated soil column by multicompartiment flow model. (In Japanese) *Proc. Environ. Sanitary Engg. Res.* 22:9–22.
- Nielsen D.R., M.Th.van Genuchten, and J.W.Biggar (1986). Water flow and solute transport processes in the unsaturated zone. *Water Resour. Res.*, 22(9): 89S–108S.
- Nkedi-Kizza P., J.W.Biggar, H.M.Selim, M.Th.van Genuchten, P.J.Wierenga, J.M.Davidson, and D.R.Nielsen (1984). On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. *Water Resour. Res.*, 20(8): 1123–1130.
- Nkedi-Kizza P., P.S.C.Rao, R.E.Jessup, and J.M.Davidson (1982). Ion exchange and diffusive mass transfer during miscible displacement through and aggregated Oxisol. *Soil Sci. Soc. Am. J.* 46:471–476.
- Parker J.C. and M.Th.van Genuchten (1984a). Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport. *Water Resour. Res.* 20(7):866–872.
- Perkins T.K. and O.C.Johnston (1963). A review of diffusion and dispersion in porous media. *Pet. Trans. AIME* 228, SPEJ 70.
- Pfannkuch H.O. (1962). Contribution a l'etude des deplacement de fluides miscible dans un milieu poreux. *Rev. Inst. Fr. Petrol.* 18(2):215.
- Rao P.S.C., R.E.Jussup, D.E.Rolston, J.M.Davidson, and D.P.Kilcrease (1980). Experimental and mathematical description of nonadsorbed solute transfer by diffusion in spherical aggregates. *Soil Sci. Soc. Am. J.* 44(4):684–688.
- Rao P.S.C., R.E.Jessup, and T.M.Addiscott (1982). Experimental and theoretical aspects of solute diffusion in spherical and nonspherical aggregates. *Soil Sci.* 133:342–349.
- Roth K., W.A.Jury, H.Fluehler, and W.Attinger (1991). Transport of chloride through an unsaturated field soil. *Water Resour. Res.* 27:2533–2541.
- Selim H.M. (1992). Modeling the transport and retention of inorganics in soil. *Adv. Agron.* 47:331–384.
- Selim H.M., J.H.Davidson, and R.S.Mansell (1976). Evaluation of a two-site adsorption desorption model for describing solute transport in soils. *Proceedings Summer Computer Simulation Conference*, Washington D.C., 444–448.
- Seyfried M.S. and P.S.C.Rao (1987). Solute transport in undisturbed columns of an aggregated tropical soil: Preferential flow effects. *Soil Sci. Soc. Am. J.* 51: 1434–1444.
- Shukla M.K. and G.Kammerer (1998). Comparison between two models describing solute transport in porous media with and without immobile water. *Austrian Journal of Water Management* 50(9/10):254–260.
- Shukla M.K., F.J.Kastanek, and D.R.Nielsen (2000). Transport of chloride through water-saturated soil columns. *The Bodenkulture, Austrian Journal of Agricultural Research* 51(4):235–246.
- Shukla M.K., F.J.Kastanek, and D.R.Nielsen (2002). Inspectional analysis of convective dispersion equation and application on measured BTCs. *Soil Sci. Soc. of Am. J.* 66(4): 1087–1094.
- Shukla M.K., T.R.Ellsworth, R.J.Hudson, and D.R.Nielsen (2003). Effect of water flux on solute velocity and dispersion. *Soil Sci. Soc. Am. J.* 67:449–457.
- Skopp J. and W.R.Gardner (1992). Miscible displacement: an interacting flow region model. *Soil Sci. Soc. Am. J.* 56:1680–1686.
- Sposito G. (1989). *The chemistry of soils*. Oxford Press, p 277.
- Taylor G.I. (1953). The dispersion of matter in solvent flowing slowly through a tube. *Proc. R. Soc. London, Ser. A* 219:189–203.

- Toride N., F.K.Leij, and M.Th.van Genuchten (1993). A comprehensive set of analytical solutions for nonequilibrium solute transport with first-order and zero-order production. *Water Resour. Res.* 29(7):2167–2182.
- Valocchi, A.J. (1985). Validity of local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resour. Res.* 21: 808–820.
- Van de Pol R.M., P.J.Wierenga, and D.R.Nielsen (1977). Solute movement in field soil. *Soil Sci. Soc. Am. J.* 41:10–13.
- van Genuchten M.Th. (1985). A general approach for modeling solute transport in structured soils. Proc. 17 The Int. Congress. IAH, Hydrogeology of Rocks of Low Permeability. Jan 7–12, 1985, Tucson, AZ. Mem. Int. Assoc. Hydrogeol. 17:512–526.
- van Genuchten M.Th. and F.N.Dalton (1986). Models for simulating salt movement in aggregated field soils. *Geoderma.* 38:165–183.
- van Genuchten M.Th. and P.J.Wierenga (1976). Mass transfer studies in sorbing porous media I Analytical solutions. *SSSA Proceedings* 40(4):473–480.
- van Genuchten M.Th. (1981). Non-equilibrium transport parameters from miscible displacement experiments. Research report 119, USD A, US Soil salinity lab Riverside, California,
- van Genuchten M.Th. and J.C.Parker (1984). Boundary conditions for displacement experiments through short laboratory soil columns. *Soil Sci. Soc. Am. J.* 48: 703–708.
- van Genuchten M.Th. and P.J.Wierenga (1977). Mass transfer studies in sorbing porous media. II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Sci. Soc. Am. J.* 41:272–277.
- van Genuchten M.Th. and P.J.Wierenga (1986). Solute dispersion coefficients and retardation factors. In: A. Klute, (ed.), *Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods*, 2nd Edition, American Society of Agronomy, Madison, Wisconsin.
- van Genuchten M.Th. and W.J.Alves (1982). Analytical solutions of the onedimensional connective dispersion solute transport equation. *USDA Tech. Bull.* 1661.
- Van Wesenbeck I.J. and R.G.Kachanowski (1991). Spatial scale dependence of in situ solute transport. *Soil Sci. Soc. Am. J.* 55:3–7.
- White R.E., L.K.Heng, and R.B.Edis (1998). Transfer function approaches to modeling solute transport in soils. In: H.M. Selim and L. Ma (eds.), *Physical nonequilibrium in soils*. Ann Arbor Press, Michigan, p 311–346.
- White R.E., J.S.Dyson, Z.Gerstl, and B.Yaron (1986). Leaching of herbicides through undisturbed cores of a structured clay soil. *Soil Sci. Soc. Am. J.* 50: 277–283.
- Wilson J.L. and L.W.Gelhar (1974). Dispersive mixing in a partially saturated porous medium, Persons Laboratory Report 191, Massachusetts Institute of Technology, Cambridge.
- Wilson G.V., H.M.Selim, and J.H.Dane (2000). Flow and transport processes. In: H.D. Scott, (ed.), *Water and Chemical Transport in Soils of the Southeastern USA*. SCSB-395. Department of Plant and Soil Sciences, Oklahoma State University.