9.1 Solute interactions

Soil Hydrology

9 TRANSPORT OF SOLUTES IN SOILS

In Chapter 3 we acknowledged that the liquid phase of a soil is never just pure water, and in Chapter 4 and subsequent chapters we rigorously defined soil water potential to include consideration of the quantity and diversity of solute species in the soil solution. Nevertheless, up to now, we did not consider the physical, chemical and biological processes within a soil profile that distribute, dilute or concentrate solute species within the liquid phase of a soil. Inasmuch as the relative concentration of solutes in the liquid phase governs not only the retention and transport of water within soils but also contributes to our understanding of managing the quality of water within soils as well as that moving below the recall of plant roots deeper into the vadose zone, we present here both microscopic and macroscopic considerations of solute behavior in soils. We limit our discussion to the soil solution and consider transport in the soil air only when it plays an important part in transport of the soil solution.

Although it has been known for at least a century that water and solutes do not travel uniformly within field soils (Lawes et al., 1881), relatively few soil hydrologists individually or collectively made a concerted effort to study and understand the topic until recent times. A few studies now considered classic kept the topic alive until the 1950s. In 1900, Means and Holmes (1901) provided a lucid description of the chemical and physical processes occurring within soils during and after rainfall and irrigation events. They understood the complexities of molecular diffusion and convection in a reactive, structured soil manifesting a heterogeneous pore size distribution. Later, Slichter (1905) noted of a water soluble chemical or "tracer" added to ground water, "its appearance ... is gradual" when measured at a downstream well. He explained that the gradual appearance of the tracer was caused by the fact that the central thread of water in each capillary pore of the soil moves faster than the water along the walls of the pore. Thirty years later, Kitagawa (1934) studying the dispersion of sodium chloride from a point source in a water-saturated sand expressed the mixing process as a function of the average pore water velocity. Approximately 10 and 20 years later, Bosworth (1948) and Taylor (1953) examined the contributions of molecular diffusion in cylindrical capillary tubes. During the succeeding forty years, investigations have accelerated owing to the growing importance of water quality. In this chapter we limit our discussion to miscible displacement - that is, when two miscible fluids are brought into contact, the initial abrupt interface between the two becomes blurred. The abrupt interface disappears owing to a mixing process dependent upon the properties of the two fluids, the properties of the porous medium, the nature of the microscopic velocity distributions of the fluids and the reactions occurring within each fluid as well as between each fluid and the porous medium.

9.1 SOLUTE INTERACTIONS

We consider here those physical interactions of solutes that play a primary role in the distribution of solutes within the soil profile.

9.1.1 Molecular Diffusion

Thermal energy provides a continual, never ending movement of gas and liquid phases of a soil system. In 1855, Fick provided a theoretical basis for this movement by showing that molecular diffusion obeyed the same mathematical laws that Newton had derived for momentum flux and Fourier for heat flux. The solid matrix of the soil complicates matters by altering both the diffusion path length and the cross sectional area available for diffusion as well as providing an electric field and reactive surfaces that further alter molecular movement.

Fick's first law of diffusion states that a gaseous or solute species moves or diffuses relative to a mixture or solution in the direction of decreasing concentration of that species just as heat flows by conduction in the direction of decreasing temperature. Hence,

$$q = -DA\frac{dC}{dx} \tag{9.1}$$

where q is the diffusive flux $[MT^{-1}]$, A the cross sectional area $[L^2]$, C the concentration $[ML^{-3}]$, x the space coordinate [L] and D the molecular coefficient $[L^2T^{-1}]$. Because concentration in a porous medium can be expressed in a number of ways, C should be of the same quantity reference as q, and the volume should be of the same length reference as x and A. Jackson et al. (1963) provide details for expressing the frame of reference as the entire bulk soil system or either one of the two fluid phases. Temperature gradients, pressure gradients and external forces also contribute to the diffusive flux. Gaseous diffusion coefficients in soil air are almost composition independent, increase with temperature and vary inversely with pressure. Coefficients in soil water depend upon concentration, solute species and usually increase with temperature. Comprehensive treatments of molecular diffusion are available (e. g. Bird et al., 1960; Crank, 1956; and Currie, 1960).



Figure 9.1 Idealized cylindrical pore within a solid matrix through which diffusion occurs.

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(9.4)

The complicated geometry of a soil relative to diffusion path length and cross sectional area is usually described in terms of two parameters - tortuosity and porosity. We assume here that isothermal conditions prevail, the bulk volume of the soil remains constant, the soil solids are inert and for convenience, we consider gaseous diffusion in one dimension within a completely dry soil schematically shown in Fig. 9.1. For steady state conditions with $C(0) = C_1$ and $C(L) = C_2$, the diffusion flux for the cylindrical pore of length L_e from (9.1) becomes

$$q = -D_o A_{\epsilon} \left(\frac{C_2 - C_1}{L_{\epsilon}} \right) \tag{9.2}$$

where D_0 is the gaseous diffusion coefficient, $A_e = APL/L_e$ the cross sectional area of the cylindrical pore, *P* the porosity and *A* the cross sectional area of the bulk soil. Similarly, for the bulk soil of length *L* (9.1) becomes

$$q = -DA\left(\frac{C_2 - C_1}{L}\right). \tag{9.3}$$

Equating (9.2) and (9.3) we have

 $D = D_o P (L / L_e)^2$

which is of a form suggested by Buckingham (1904) where $(L/L_e)^2$ is the called tortuosity and equals $cos^2\alpha$. Penman's (1940) commonly used value of $(L/L_e)^2 = 0.66$ yields an angle of 0.61 or 35° between the pore and the solid particle of soil. Marshall (1958) and Millington and Quirk (1959) empirically raised the power of P to 3/2 and 4/3, respectively, and deleted $(L/L_e)^2$ in (9.4) to account for the tortuosity of the average diffusion path.

Equations similar to (9.4) are easily derived for diffusion coefficients in partially water saturated soil as well as for solute diffusion in saturated and unsaturated soils. For example, Sallam et al. (1984) experimentally showed that the product $P(L/L_e)^2$ in (9.4) for gaseous diffusion in unsaturated soils is more nearly equal to $a^{3.10}P^{-2}$ rather than $a^{10/3}P^{-2}$ (Millington and Quirk, 1959) where a is the air-filled porosity. Even for isothermal conditions, in addition to the concentration gradient, we have oversimplified our discussion here by neglecting pressure gradients and external forces acting unequally on the various gaseous and solute species. And, we should remember that the value of a diffusion coefficient depends upon the nature of the counter-diffusing gaseous or solute species.

9.1.2 Electrostatic and Electrokinetic Forces

Electric force fields always exist within the pore structure of soils owing to the electric charge possessed by the walls of soil pores. The charge per unit pore wall area is caused by isomorphous substitution of atoms in the tetrahedral and octahedral layers of the clay minerals as well as the presence of the Si-O-H (silanol) group on quartz, kaolin minerals and other surfaces like organic matter (-OH and -COOH). The magnitude of the former is fixed while that of the latter depends upon pH and concentration of the soil solution. In general, small highly charged ions cause the viscosity of the soil solution to increase while

large monovalent ions cause the viscosity to decrease. The electrostatic fields of the ions cause polarization and a binding of surrounding water molecules which alter the kinetic properties of soil water. The hydrophilic nature of most soil particles is attributed to the attraction of hydrated cations by the electrostatic field of soil particles and to the hydrogen bonding of water to the clays (Low, 1961). The mobility of both water and ions in the region of the pore walls is reduced below that in bulk solutions (Kemper, 1960; and Dutt and Low, 1962). The impact of the electric field on ions and water is more pronounced in clayey soils and depends upon the ionic concentration and distance from the pore wall.



Figure 9.2. Distributions of cations and anions in the vicinity of a clay particle surface for three different solution concentrations.

Gouy (1910) described the distribution of cations as a function of distance from a negatively charged flat surface by equating the electrostatic force causing cations to move toward the surface to that from their thermal motion causing them to diffuse away from the surface. We see in Fig. 9.2 that the extent of the unequal distribution of cations and anions away from the surface depends inversely upon the total concentration C_o of the solution. And, we note from Fig 9.3 for cylindrical pores with a wall having a net negative charge and filled with a solution of concentration C_o that the concentration distribution across the pores depends upon the magnitude of the pore radius. In the center of large pores the concentrations of cations and anions are identical while in the center of small pores owing to the electric field, the cationic concentration exceeds that of anions.





When redistribution of soil water occurs by air entering larger waterfilled pores, solutes within water films remaining in the "emptied" large pores diffuse and mix with those in water-filled smaller pores achieving a new equilibrium which manifests different concentration distributions in all pores large and small. Recognizing that the rates of water and solute redistribution are interdependent, equilibrium distributions of solute and water (hysteresis) both depend upon the rate at which hydraulic equilibrium is reached (Davidson et al., 1966).

As water moves through pores, cations and anions unequally distributed across the pores because of the negatively charged pore walls are swept along with the water. Consequently, a differential charge builds up along the length of flow which tends to retard water flow. This differential charge is called streaming potential. Similarly, if an electrical potential difference is established across a soil, ions moving within the electric field will create a water flux. Analytical descriptions of streaming potential, electroosmosis, electrophoresis and sedimentation potential are found in the literature (e.g. Nerpin and Tchudnovskii, 1967, and Taylor and Ashcroft, 1972). Each process contributes to the behavior of solutes and water at the pore scale and offers an opportunity for understanding and managing solute movement and retention in soil profiles.

9.1.3 Other Reactions

Constituents in the gas, liquid and solid phases of soil continually reacting with each other through a variety of chemical and biological pathways contribute to the presence and behavior of particular solutes in soil profiles. Applicable equilibrium and nonequilibrium chemical concepts such as oxidationreduction, solubility-precipitation, association-dissociation, acid-base and exchange-adsorption are described by Freeze and Cherry (1979) and Luckner and

9.2 Miscible displacement in a capillary

Schestakow (1991). Descriptions of microbiological reactions and pathways are available (e. g. Bazin et al., 1976) as well as those involving root systems of higher plants (e. g. Nye and Tinker, 1977). A full understanding of solute transport requires a knowledge of the information contained in these and other references.

9.2 MISCIBLE DISPLACEMENT IN A CAPILLARY

The oldest approach to analytic descriptions of miscible displacement in soils and other porous media is that of the displacement of a fluid by a second miscible fluid within a capillary tube. Consideration was focused upon the average displacement velocity and geometric boundaries with little concern for chemical or microbial processes.

9.2.1 Displacement without Molecular Diffusion

From the definition of viscosity, the force per unit area τ required to shear a fluid of viscosity η is

$$\tau = -\eta \, \frac{dv}{dr} \tag{9.5}$$

where v is the velocity of the fluid and r the coordinate normal to the force. The velocity distribution within a horizontal capillary tube of radius a during steady, uniform flow caused by a pressure difference Δp across its length L is the result of an equilibrium between the pressure and shearing forces acting on the fluid. Hence, for the capillary tube

$$\pi r^2 \Delta p + 2\pi r L \eta \frac{dv}{dr} = 0 \tag{9.6}$$

Integrating (9.6) between the limits r = r and r = a (where v = 0), we have the well known parabolic velocity distribution

$$v(r) = 2v_o \left(1 - \frac{r^2}{a^2} \right)$$
(9.7)

where $v(0) = v_0 \cdot t_0 \cdot t_0 \cdot t_0 \cdot t_0 \cdot t_0$ The volumetric flow rate Q (cm³·s⁻¹) through the capillary is easily obtained by integrating v(r) with the areal **cmass** section of the capillary

$$Q = \int_0^a 2\pi r v(r) dr = 4\pi v_o \int_0^a (r - r^3 / a^2) dr$$
(9.8)

or

$$Q = a^2 \pi v_o = \frac{a^* \pi \Delta P}{8 \eta L}.$$
(9.9)

And the average velocity \overline{v} of fluid flowing within a capillary tube is simply

$$\overline{v} = \frac{1}{\pi a^2} \int_0^a 2\pi r v(r) dr = \frac{4v_o}{a^2} \int_0^a (r - r^3 / a^2) dr$$
(9.10)

which leads to $\overline{v} = v_o$.

If we assume no molecular diffusion and rely solely on (9.7) to describe the fluid velocity, what will be the distribution of a second fluid of concentration C_o as it displaces a fluid of zero concentration initially within a capillary? Consider the solution C_o enters the tube at x = 0 at time t = 0. The concentration C averaged over the cross section of the capillary at distance x is

$$C_a = \frac{1}{\pi a^2} \int_0^a 2\pi r C(r) dr$$

or as a function of distance and time is

$$C_{a}(x,t) = C_{o}(1-x/2v_{o}t).$$
(9.11)



Figure 9.4. Parabolic velocity distributions of an invading solution C₀ within a capillary (upper) give rise to linear average concentration distributions along the tube (lower).

In Fig. 9.4, the paraboloid of the displacing fluid C_o within the capillary gives rise to a linear concentration distribution. When the invading front of C_o has reached a distance 2L, the average concentration across the plane normal to the capillary at a distance of L is $C_o/2$. Interestingly, the average concentration of the fluid moving across the plane L at that instant is not $C_o/2$ but $3C_o/4$. The average concentration of fluid moving past x = L (see Fig. 9.5a) is

$$C_{a} = \frac{mass of solute moving past x = L}{volume of fluid moving past x = L}$$

$$C_{a} = \frac{C_{o} \int_{0}^{r'} \left[2v_{o} \left(1 - r^{2} / a^{2} \right) \right] 2\pi r dr}{\int_{0}^{a} \left[2v_{o} \left(1 - r^{2} / a^{2} \right) \right] 2\pi r dr}$$
(9.12)

t where $r' = a(1 - L/2v_o)^{1/2}$, the radial boundary between the displacing fluid ($C = C_o$ for r < r') and the original fluid (C = 0 for r > r'). Integrating (9.12) leads to $C_a(t)/C_o = 0$ $v_ot/L \le 0.5$ (0.10)

$$= 1 - L^2 / 4 v_o^2 t^2 \qquad v_o t / L > 0.5$$
(9.13)

or

$$C(p) / C_o = 0 \qquad p \le 0.5 = 1 - 1 / 4p^2 \qquad p > 0.5$$
(9.14)

where $p = v_o t/L$ and is the ratio of the volume of fluid passing x = L to the volume of the capillary between $0 \le x \le L$. Pore volume of effluent or simply pore volume is the name commonly used for p. The value of $C = 3C_o/4$ for p = 1 and approaches unity as $p \to \infty$, see Fig. 9.5b. Even for such a simple geometry as a capillary tube, the concentration distribution within the tube (Fig. 9.4b) is not easily reconciled with the shape of the concentration elution curve (Fig. 9.5b).





9.3 Miscible displacement in surrogate porous media

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9.2.2 Displacement with Molecular Diffusion

Taylor (1953) provided insights to separate dispersion of a solute within a capillary caused by molecular diffusion from that by the velocity distribution of the fluid. Assuming that the solute concentration within a capillary is symmetric about its central axis and the velocity of the fluid is described by (9.7), the mixing of a solute by both diffusion and convection are described by

$$\frac{\partial C}{\partial t} = D_m \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2} \right) - 2v_o \left(1 - \frac{r^2}{a^2} \right) \left(\frac{\partial C}{\partial x} \right)$$
(9.15)

where we assume the molecular diffusion coefficient D_m is independent of concentration. The following initial and boundary conditions approximate our assumption that the displacing solution C_o enters a long capillary at a uniform rate at x = 0 starting at time t = 0:

C=0	t=0	x>0	0 <r<a< th=""><th></th></r<a<>	
$C = C_o$	<i>t</i> ≥0	x=0	0 <r<a< td=""><td></td></r<a<>	
C=0	<i>t</i> ≥0	$x \rightarrow \infty$	0 <r<a< td=""><td>(9.16)</td></r<a<>	(9.16)
$\frac{\partial C}{\partial x} = 0$	<i>t</i> ≥0	0< <i>x</i> <∞	r=0 and $r=a$	

Details of a numerical solution of (9.15) subject to (9.16) are given by Amanthakrishnan et al. (1965). The limiting case for a very small fluid velocity when $v \rightarrow 0$ is the analytic solution

$$(C / C_o)_a = erfc \left[\frac{x}{\sqrt{4Dt}} \right]$$
(9.17)

where erfc is the complementary error function defined by

$$erfc(z) = \frac{2}{\sqrt{\pi}} \int_{z}^{\infty} \exp(-\alpha^{2}) d\alpha$$
 (9.18)

For small velocities considerably greater than zero, Taylor (1953) assumed that solute mixing by longitudinal molecular diffusion could be neglected compared with that owing to convection and suggested an alternative experimental procedure for measuring the molecular diffusion coefficient. Assuming that $\partial^2 C / \partial x^2 = 0$ in (9.15), making the Galilean transformation $[x_1 = (x - v_0 t)]$ to change the coordinate from the cylinder to the fluid and further assuming that

$$\frac{\partial (C/C_o)_a}{\partial x_1} = \frac{\partial (C/C_o)_{x_1}}{\partial x_1},$$

he found that the flux density of solute at x_1 is

q

$$= -\frac{a^2 v_o^2}{48 D_m} \frac{\partial C}{\partial x_1}.$$
(9.19)

This equation shows that a solute is dispersed relative to a plane which moves with a velocity v_0 exactly as though it were being mixed by molecular diffusion [compare with (9.1)] but with an apparent diffusion coefficient D_a defined by

$$D_{a}=\frac{a^{2}v_{o}^{2}}{48D_{m}}.$$

(9.20)

Aris (1956) extended the above analysis for irregularly shaped capillaries which also included the mixing contribution from longitudinal molecular diffusion. His analysis, allowing a non parabolic local velocity distribution within the irregular capillaries and a concentration-dependent molecular diffusion coefficient, gives the apparent diffusion coefficient

$$D_a = D_m + \frac{\alpha \bar{a}^2 \bar{v}_o^2}{D_m} \tag{9.21}$$

where α is a dimensionless number which depends upon the cross section, \overline{a} the effective radius and \overline{v}_{o} the mean flow velocity.



Figure 9.6. Spreading or dispersion of a solute caused by convective transport in a simplified soil a. and a 2-dimensional network of square soil particles b.

9.3 MISCIBLE DISPLACEMENT IN SURROGATE POROUS MEDIA

The mixing and interactive processes described in section 9.1 for simple, welldefined geometries and materials provide a basis for understanding transport in soils. Unfortunately, the rigor of solutions exemplified by those of Taylor (1953) gives way to that of empirical or statistical formulations owing to our inability to mathematically define the geometry of the soil pore system or to measure parameters descriptive of the displacement processes that can be translated from the pore scale through intermediate scales (including that of a REV) to that of a pedon or field. Miscible flow in a porous medium differs from that in a single capillary owing to meandering paths of water and solutes within and between irregularly shaped pores. The spreading or dispersion of the solute caused by convective transport with the water can be qualitatively visualized in Fig. 9.6a for a simplified soil, or in Fig. 9.6b for an idealized 2-dimensional network of square soil particles. In both figures, the invading stream of solute partitions itself according to the microscopic pore water velocities occurring between the soil particles. At still a smaller scale, the water velocity is zero at the particle surface, departs markedly from the mean flow direction and approaches a zero value in the vicinity of dead-end pores (Fig. 9.7). These pathways and pore water velocities, severely altered with slight changes of water content, have yet to be quantitatively evaluated. In the near future, computer-aided micro tomography and nuclear magnetic resonance techniques will provide an opportunity to ascertain the exact nature of the velocities at the pore scale. Without such observations, our understanding of certain facets of miscible displacement in soils has been enhanced by considering surrogate porous media having simplified or empirical pore geometries. These equations developed to describe the displacement of fluids in such media are usually deficient of physical and mathematical rigor at the pore scale and often contain empirical coefficients not easily related to natural soils.



9.3.1 Displacement in Capillary Networks

Descriptions of idealized soil pores having capillary shapes include some mechanism for transport between parallel capillaries or allow one or more capillary tubes of differing radii to be joined at their ends at common junctions (e. g. Marle and Defrenne, 1960). The concept of random networks of capillary tubes provides insights to the meandering paths of displacing fluids.



Figure 9.8. Diagram of pore space. a. Tetrahedral pore between four spheres, b. pore schematized by a canal bifurcation and c. random path chosen by a solute particle through the canal system.

The capillary tube network (de Josselin de Jong, 1958) illustrated in Fig. 9.8 stems from the tetrahedral pore between four closely packed spheres being represented by a junction of four capillaries. The randomness of the capillaries originates from the assumption that their positions are dictated by a random arrangement of soil particles. With z being the direction of principal flow, the direction of each segment of the capillary network is described by the angles α_1 and α_2 . de Josselin de Jong neglected molecular diffusion and assumed that the velocity of a fluid particle was that of the mean velocity across the capillary diameter. Assuming that every capillary segment is of length l and the fluid velocity within each segment i is $t_i = t_R/\cos \alpha_2$ where t_R is the minimum residence time of a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a segment oriented in the direction of principal flow. Hence, a fluid particle traveling in a seg

(9.22)

(9.23)

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$$\Delta r = \frac{l \Delta t \sin \alpha_2 \cos \alpha_2}{t_2}.$$

These deviations lie on a sphere centered at $l \Delta t/2t_R$ having a radius $l \Delta t/2t_R$.

The dispersion of many fluid particles having passed through a large number of capillary segments resembles that of Brownian movement, but translated in the direction of the principal flow. Hence, the maximum concentration of an injected solute travels at the mean velocity of the fluid $l/(3t_R)$. With this simple capillary network composed of segments of invariant length, de Josselin de Jong was the first to show that the transverse apparent diffusion coefficient is smaller than the longitudinal apparent diffusion coefficient. He also showed that the magnitude of the longitudinal apparent diffusion coefficient depends upon the distance traveled. Subsequently, Saffman (1959, 1960) derived a similar, but more general model where the path of the fluid particle was regarded as a random walk with the direction, length and duration of each step being random variables. He accounted for pure molecular diffusion and the interaction between molecular diffusion and fluid convection.

9.3.2 Miscible Displacement as a Random Walk Process

Statistical concepts have been applied to solute and water transport through porous media at the pore scale primarily because of the difficulty of integrating differential equations of motion with poorly or undefined complex boundary conditions. Danckwerts (1953), Scheidegger (1954) and others have assumed that a simple random walk stochastic process can be used to describe transport in a fluid-saturated homogeneous, isotropic porous medium generally considered chemically inert. Here the exact nature of the path followed by fluid particles theoretically obeying Navier-Stokes equation in the porous system is not known. The velocity or position of a water or solute particle is the random variable and as the particle passes through the porous system, it eventually encounters all situations that are possible at any one given time. The probability distribution function w for any water particle at various points along the random path (Scheidegger, 1954) is given by



where v_x , v_y and v_z are the Darcy velocity components [components of q in (5.32) each divided by θ] in directions x, y and z, and $D = \sigma^2/2t$ where σ^2 is the variance of w(x, y, z, t). Day (1956) described in detail the connection between w(x, y, z, t) and the macroscopic concentration of a solute being displaced in a saturated sand.

Recognizing that (9.24) is proportional to the solute concentration and knowing that (9.24) satisfies classical diffusion equations, Danckwerts (1953)

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used solutions of

 $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}$

(9.25)

subject to appropriate initial and boundary conditions to describe the displacement of solutes through fluid-saturated porous media where $X = (x - v_x t)$. He noted that the value of *D* must be determined empirically and would presumably depend upon the viscosity, density and velocity of the fluid, and on the size and shape of the solid particles. He called *D* the "diffusivity" while Scheidegger named it the "factor of dispersion".

9.3.3 Displacement in a Representative Elementary Volume

The random capillary models described above were made somewhat more physically realistic [Bear and Bachmat, 1967] by deriving the idea of a representative elementary volume at the macroscopic scale from microscopic quantities at the pore scale averaged over many pores. Molecular diffusion and convection of solutes and water flowing within individual pores are described at the pore scale while the spreading or dispersion of solutes with water as it curves around and between soil particles through sequences of pores occurs at the macroscopic scale.

Bear and Bachmat envisioned the porous medium as a network of randomly interconnected narrow channels of varying length, cross section and orientation. The chemically inert, non compressible liquid of variable viscosity and density saturating the pores obeys Poiseulle's law and has two components a solvent and a solute. No surface phenomena between the solid particles and the liquid take place. After deriving and averaging mass conservation and movement equations for the liquid in and across a channel, these local equations were averaged in a REV to obtain macroscopic equations. Details of all assumptions and the various averaging processes that lead to macroscopic equations containing average non random variables and parameters assigned to the centroid of the REV are given by Bear (1969). We repeat here their final equation of mass conservation in one direction avoiding the second-rank tensorial notation necessary for a three dimensional analysis

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\left(D_c + D_m \right) \frac{\partial C}{\partial x} \right] - \frac{\partial (vC)}{\partial x}$$
(9.26)

where v and C are average values within the REV and D_c and D_m are the coefficient of convective (or mechanical) dispersion [L T⁻²] and coefficient of molecular diffusion [L T⁻²], respectively. Combining the latter coefficients into a single term D_a (commonly called the hydrodynamic dispersion coefficient or the apparent diffusion coefficient), we have

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D_a \frac{\partial C}{\partial x} \right] - \frac{\partial (vC)}{\partial x}$$
(9.27)

for which many investigators have sought theoretical or experimental

relationships between the value of D_a (which embraces solute mixing at both the pore scale and the pore-sequence scale within an REV) and the value of v (the average pore water velocity usually estimated by the ratio of the Darcian flux density and water content θ).

The results of several studies summarized by Pfannkuch (1962) related the value of D_a to the Peclet number of molecular diffusion Pe equal to vd/D_m where d is the mean solid particle size or other characteristic length of the porous medium. Recognizing that the effects of both molecular diffusion and convection on solute mixing in typical one-dimensional experiments were difficult separate, Fried and Combarnous (1971) suggested five ranges of Peclet numbers or zones to delineate the relative magnitudes of each process. For laboratory or field soils, we suggest that the following four zones will generally suffice except under some field conditions when turbulent flow down large fissures and cracks prevails during periods of rapid infiltration:

Zone 1 Zone 2 Zone 3	Pe < 0.3 0.3 < Pe < 5 5 < Pe < 20	$D_a = D_m$ $D_a = (D_m + D_c)$ $D_a \leq (D_m + D_c)$	$D_c \ll D_m$ $D_c \approx D_m$
Zone 4	Pe < 20	$D_a = D_c$	$D_c > D_m$ $D_c > D_m$
RELATIVE Cl ³⁶ CONC. C/ C _o	PORE VOLUN 390μ GLASS BEADS 000 v = 7.80 cm·hr ⁻¹ 000 v = 0.499 cm·hr ⁻¹	$D = 1.59 \cdot 10^{-100}$ $D = 5.75 \cdot 10^{-5}$ 1.0 AE OF EFFLUENT) ⁻⁵ cm· s ⁻¹ .m· s ⁻¹

Figure 9.9. Breakthrough curves of ³⁶Cl for the displacement of 0.10 N NaCl at two flow rates through a uniform column of glass beads.

Zones 1 and 2 are illustrated in Fig. 9.9 for a miscible displacement experiment conducted with a column uniformly packed with 390 μ glass beads initially saturated with 0.10 N NaCl. This initial solution was displaced at two different pore water velocities (0.499 and 7.80 cm h⁻¹) with a chemically identical solution containing Na³⁶Cl to observe the mixing process and to match the concentration distribution measured at x = 30 cm with the solution of (9.27) subject to conditions

C = 0	x > 0	<i>t</i> = 0	
C = C₀	x = 0	<i>t</i> > 0	(9.28)
C = 0	$x \rightarrow \infty$	$t \ge 0$	

where C_o is the concentration of ³⁶Cl. For each of the two pore water velocities, Fig. 9.9 shows measured values of the relative concentration C/C_o and smooth curves satisfying (9.27) and (9.28) fitted to the data through the selection of the only unmeasured entity D_a in

$$\frac{C(x,t)}{C_o} = erfc\left(\frac{x-vt}{\sqrt{4D_a t}}\right) + \exp\left(\frac{vx}{D_a}\right)erfc\left(\frac{x+vt}{\sqrt{4D_a t}}\right)$$
(9.29)

where erfc the complementary error function has been defined earlier by (9.18). Values of D_a for each value of v satisfy the equation (Fried and Combarnous, 1971)

$$\frac{D_a}{D_m} = 0.67 + \alpha \left(\frac{vd}{D_m}\right)^n \tag{9.30}$$

where $D_m = 1.98 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Wang, 1952) and $d = 3.9 \cdot 10^{-2} \text{ cm}$. Experimentally determined values of $\alpha = 0.51$ and n = 1.02 agree with those suggested by Fried and Combarnous (1971). For the slower pore water velocity (0.499 cm·h⁻¹) with Pe = 0.27 (corresponding to the upper end of Zone 1), 83% of the mixing is caused by molecular diffusion. For the faster velocity (7.80 cm·h⁻¹) with Pe = 0.43 (corresponding to the lower end of Zone 2), only 23 % of the mixing is caused by molecular diffusion.

Equation (9.30) is frequently reduced to

 $D_{a} = 0.$

$$67 D_m + \beta v^n$$

for Zones 3 and 4 with the molecular diffusion term neglected and the value of n taken as unity. In such instances, β is called the dispersivity.

Various investigators have used (9.27) or many similar diffusion type equations such as (9.25) with particular assumptions regarding the role of longitudinal and transverse molecular diffusion to theoretically or experimentally relate D_a to some function of v such as (9.30) or (9.31). Twenty five years ago Simpson (1969), writing a review article on the relationship between pore water velocity and the value of the longitudinal dispersion coefficient, stated, "The critical experiments remain to be performed: a systematic investigation of the effect on dispersion of changes in the molecular diffusivity". Somewhat later Sposito et al. (1979) presented a critical review of different theories used to describe solute transport through porous media. His remarks relative to theories based upon fluid mechanics and kinematic approaches employing various statistical techniques reveal major opportunities

to improve our understanding of miscible displacement in surrogate porous materials. Earlier reviews by Fried and Combarnous (1971) and Bear (1969) also provide additional insights for future research.

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(9.31)

9.4 One-dimensional laboratory observations

9.4 ONE-DIMENSIONAL LABORATORY OBSERVATIONS

The displacement of one fluid by another miscible fluid in a soil studied either in the laboratory or the field offers theoretical and experimental challenges that have only partially been explored despite 30 years of recent investigation. For water infiltrating into a deep, homogeneous, water-saturated soil, we see in Fig. 9.10 that a solute of concentration C_o maintained at a point on the soil surface is dispersed vertically and horizontally. The velocity of the soil solution varies in both magnitude and direction owing to the distribution of irregularly shaped pores within the soil. Along transect A-A', the initial concentration C_o at z = 0gradually diminishes to zero. Similarly, the concentration distribution normal to the average flow along transect B-B' gradually broadens with soil depth.



Figure 9.10. A solution of concentration C₀ being introduced at one point on the surface of a uniform, water-saturated soil during steady state infiltration. Right: Concentration distribution along vertical transect A-A'. Bottom: Concentration distribution along horizontal transect B-B'.

One dimensional soil columns studied in the laboratory provide a simple means of quantifying the mixing, spreading or attenuation of the solute schematically presented in Fig. 9.10. An apparatus is required to maintain steady state flow and invariant soil water content conditions when the initial soil



Figure 9.11. Laboratory apparatus for conducting miscible displacement experiments.

solution is invaded and eventually displaced by a second miscible solution. No mixing of the two solutions should occur at their boundary before entering the soil column, and samples of effluent to be analyzed for solute concentration has to be collected without disturbing the steady state flow conditions. A cross sectional sketch of a typical apparatus is given in Fig. 9.11. Details of its construction and operation are available (e. g. Nielsen and Biggar, 1961).

9.4.1 Breakthrough Curves

Without first considering specific physical, chemical or biological mechanisms involved in miscible displacement, much can be learned from a general description of continuous flow systems (Danckwerts, 1953). Let the volume of the soil column occupied by soil solution be V_o [L³] and the rate of inflow and outflow of the soil solution be Q [L³ T¹]. If the initial soil solution identified by a solute concentration C_i is suddenly displaced by an incoming solution C_o , the fraction of this incoming solute in the effluent at time t [T] will be $(C - C_i)/(C_o - C_i)$, or for an initial concentration of zero, simply C/C_o . Plots of C/C_o versus pore volume of effluent (Qt/V_o) , commonly called breakthrough curves, describe the relative times taken for the incoming solution to flow through the soil column. Note that the definition of pore volume of effluent is not restricted to water-saturated conditions but is applicable to all soil water contents. Any experimentally measured breakthrough curve may be considered one or a combination of any of the five curves shown in Fig. 9.12.

For Fig. 9.12a-c, the solute spreads only as a result of molecular diffusion and microscopic variations of the velocity of the soil solution, i. e. there is no interaction between the solute, water and soil particle surfaces. In these cases

 $\frac{Q}{V}\int_0^\infty (1-C/C_o)dt = 1$ (9.32)

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regardless of the shape of the curve. This equation expresses the fact that the original soil solution occupied exactly one pore volume or that the quantity of solute within the soil column that will eventually reach a chemical equilibrium with that in the influent and effluent is $C_o V_o$. Note also that the area under the breakthrough curve up to one pore volume (area A in Fig. 9.12b and c) equals that above the curve for all values greater than one pore volume (area B), regardless of the shape of the curve. This latter statement is a direct result of (9.32), i. e.

$$\frac{Q}{V_o} \int_0^{V_o/Q} (C/C_o) dt = \frac{Q}{V_o} \int_{V_o/Q}^{\infty} (1 - C/C_o) dt.$$
(9.33)

Danckwerts (1953) defined holdback H_b as the left hand term of (9.33) having a range $0 \le H_b < 1$ for non reacting solutes. The concept of holdback is a useful qualitative description whenever interactions between solute, water and soil solids are minimal. It indicates the amount of the soil water or solutes not easily displaced. Values of H_b for unsaturated soils have been evaluated to be 3 to 4 times greater than those for saturated soils.





Piston flow (Fig. 9.12a) never occurs owing to solute mixing that takes place by molecular diffusion and variations in water velocity at the microscopic level within soil pores. A breakthrough curve obtained from a water-saturated Oakley sand (Fig. 9.13a) is characteristic of the longitudinal dispersion shown in Fig. 9.12b. Evidence for lack of solute-solid interaction is the fact that the areas described by (9.33) are nearly identical. A water-saturated soil composed of equalsized aggregates manifesting a bimodal pore water velocity distribution yields the breakthrough curve given in Fig. 9.13b that illustrates the curve of Fig. 9.12c. With the areas of (9.33) for this curve being comparable, any interaction between the solute and the soil particles is negligible.



Figure 9.13. Chloride breakthrough curves for water-saturated a. Oakley sand and b. Aiken clay loam.

Figure 9.14 presents breakthrough curves for Cl⁻ and tritium (as tritiated water) from Columbia silt loam at two water contents and an average pore water velocity of approximately 0.4 cm h⁻¹. At a saturated water content of 0.482 cm³·cm⁻³ (Fig. 9.14a), the Cl⁻ curve was measured to the left of one pore volume (given by the vertical broken line) and the tritium curve to the right of one pore volume. The translation of the Cl⁻ curve to the left of one pore volume is characteristic of the curve in Fig. 9.12d and results from the repulsion of the negatively charged Cl ions from the negatively charged soil particle surfaces. The translation of the tritium curve to the right of one pore volume is characteristic of the curve in Fig. 9.12e and results from adsorption and exchange of tritium in the soil. Despite these different interactions, the close proximity of the curves at $C/C_0 = 0$ and their relative shapes near $C/C_0 = 1$ indicate the more complete mixing of the tritium having the greater molecular diffusion coefficient. A solute having the greater diffusion coefficient mixes more completely with the water in stagnant and slowly conducting zones, thus delaying its appearance in the effluent. In this case, the initial breakthrough of the solute having the greater molecular diffusion coefficient is translated to the



Figure 9.14. Chloride and tritium breakthrough curves for Columbia silt loam at soil water contents a. 0.482 cm³·cm⁻³ and b. 0.472 cm³·cm⁻³. The vertical broken lines designate 1 pore volume.

right of that of the other solute. It should not be expected that the relative behavior of solutes described above would be the same for all velocities and different soils. For example, if one solute has a diffusion coefficient much greater than the other, it would be possible for it to not only invade the nearly stagnant zones but also diffuse downstream ahead of the other solute. In this case the faster diffusing solute will appear in the effluent earlier that the more slowly diffusing solute.

In Fig. 9.14b, decreasing the water content by only 0.01 cm³ cm⁻³ translated both Cl⁻ and tritium curves to the left of one pore volume. Unsaturating the soil alters the pore water velocity distribution, allows some of the solute to arrive downstream earlier and increases the magnitude of holdback manifested by area A in Fig. 9.12. Desaturation eliminates larger flow channels and increases the volume of water within the soil which does not readily move. These almost stagnant water zones act as sinks to molecular diffusion. Later we shall discuss the opportunity afforded by controlling the water content and pore water velocity to change the leaching efficiency of field soils.

A more illustrative example of curves b, c and d in Fig. 9.12 are given in Fig. 9.15 from two columns of Oakley sand initially fully saturated with Ca^{2+}





Figure 9.15. Chloride and magnesium breakthrough curves for initially Casaturated Oakley sand at soil water contents a. 0.327 cm³·cm⁻³ and b. 0.235 cm³·cm⁻³. The two vertical, broken lines designate 1 pore volume for the chloride and the cation exchange capacity, respectively.

[cation exchange capacity of 3.75 me (100g)⁻¹] and 0.1 N calcium acetate flowing through them at a constant velocity while maintaining a constant water content. Breakthrough curves of Cl⁻ and Mg²⁺ for 0.10 N MgCl₂ displacing the calcium solution at water contents of 0.327 and 0.235 cm³·cm⁻³ are presented in Fig. 9.15a and 9.15b, respectively. The positions of the Cl⁻ curves appear in the vicinity of the vertical lines representing the volume of solution in each soil column, while those of Mg²⁺ appear further to the right in the vicinity of another vertical line accounting for the cation exchange capacity. For the greater soil water content (Fig. 9.15a) the Mg^{2+} curve has the same characteristics as the Cl⁻ curve (similar to Fig. 9.12b) even though it is flatter and is displaced to the right (similar to Fig. 9.12d). Desaturating the soil water content (Fig. 9.15b) produces a CI⁻ curve similar to Fig. 9.12c and a Mg²⁺ curve having the shape of Fig. 9.12c but a position illustrated in Fig. 9.12d. Depending upon the concentration and velocity of the displacing solution and the prevailing soil water content, the shapes and positions of breakthrough curves are governed by the characteristics of the cation exchange process as well as the mixing which occurs by the pore water velocity distribution, molecular or ionic diffusion and the spatial and temporal interaction of these processes.



Figure 9.16. Breakthrough curves of ³⁶Cl for 0.01 N NaCl displacing 0.01 N NaCl and for 4.0 N NaCl displacing 4.0 N NaCl in horizontal columns of watersaturated glass beads.

9.4.2 Magnitude of the Diffusion Coefficient

The majority of inorganic cations, anions and solutes in soil solutions have diffusion coefficients in the order of 10^{-5} cm²·s⁻¹ while organic cations, anions and solutes usually manifest much smaller values. These coefficients are moderately temperature dependent and slightly concentration dependent. The importance of their different magnitudes is apparent only at relatively small pore water velocities and often difficult to measure except under rigorously controlled laboratory conditions.

For a 30-cm long column of 390 μ glass beads, the results of two experiments observing the displacement of 0.01 N NaCl by an identical solution identified with a tracer of ³⁶Cl⁻ and the displacement of 4.00 N NaCl by a similarly observed identical solution containing ³⁶Cl⁻ are given in Fig. 9.16. With the pore water velocity for each experiment conducted at 25 ±1°C being about 0.48 cm·h⁻¹ (Zone 1 described in section 9.3.3) and the densities and viscosities of the displacing and displaced solutions being virtually identical, distinctly separate curves for each experiment are obtained owing primarily to the different self diffusion coefficients of ³⁶Cl⁻ (1.98·10⁻⁵ and 1.24·10⁻⁵ cm²·s⁻¹ for the concentrations of 0.01 and 4.00 N NaCl, respectively). At greater pore water velocities (Zones 2 through 4) where mixing by convection progressively dominates the displacement process, the importance of diffusion lessens. Accordingly, for most infiltration and redistribution events following rainfall or irrigation in field soils, a nominal value of the diffusion coefficient is assigned to either an inorganic or organic solute without discriminating between solute species or their concentrations. The impact of temperature on diffusional mixing remains obscure from investigation.

9.4 One-dimensional laboratory observations

9.4.3 The Impact of Density and Viscosity

The existence of concentration gradients of inorganic salts in the soil solution responsible for solute transfer by diffusion or as a result of convection guarantees that the displacing and displaced solutions do not generally have identical values of density or viscosity no matter how close their values. In soils, it is not uncommon to experience solutions of unequal density and viscosity. During the extraction of water from soil profiles by plants or by evaporation at the soil surface, the density and viscosity of the soil solution increase continually. Conversely the infiltration of rain or many irrigation waters causes the soil solution to be diluted. Fertilizers and other agrochemicals also alter these properties of the soil solution. The density and viscosity of the soil solution also differ from those of the bulk solution owing to the interaction of water and the soil particle surfaces especially in unsaturated soils or those soils having large clay contents (Dutt and Low, 1962).

When two superposed solutions of unequal density are accelerated in a direction perpendicular to their interface, the surface may be stable or unstable. Differences in density provide unbalanced forces while differences in viscosities account for unequal drag forces. For example, unstable flow occurs for particular velocities vertically downward when a dense, more viscous fluid displaces a less dense, less viscous fluid. Here, the unbalanced forces tend to accèlerate the denser fluid into the less dense fluid below with the viscous drag of the lower fluid unable to counter-balance this acceleration. With this action "fingers" of the more viscous fluid invade those pore sequences occupied by the less dense fluid. For a 30 cm long vertical column of 390 μ glass beads, the breakthrough curve in Fig. 9.17 obtained for 0.01 N NaCl flowing upward at a velocity of 6.07



Figure 9.17. Breakthrough curves of ³⁶Cl for 0.01 N NaCl displacing 0.10 N NaCl vertically upwards at two different flow velocities in columns of watersaturated glass beads. The broken line is a breakthrough curve for stable flow similar to that in Fig. 9.16.

9.4 One-dimensional laboratory observations

 $cm \cdot h^{-1}$ and displacing the more dense and viscous 0.10 N NaCl exhibits unstable flow compared to that for stable flow (a curve from Fig. 9.16 shown as a broken line).

The stability of the displacement depends upon the viscosities and densities of the fluids, the permeability of the soil, and the direction and velocity of the displacement. If Darcy's equation is obeyed for steady movement with average pore water velocity v vertically upwards through a soil of permeability K_{v} , the interface between the two solutions will be unstable for

$$(\mu_2 - \mu_1)v + K_n(\rho_2 - \rho_1)g < 0 \tag{9.34}$$

where ρ is the density, μ the viscosity and g the gravitational acceleration (Taylor, 1950). The subscripts 1 and 2 refer to the displaced and displacing fluids, respectively. Except for signs owing to the direction of the velocity, (9.34) also applies to movement vertically downward. Inequality (9.34) has been used extensively for immiscible fluids (e.g. Oatmans, 1962) and for miscible fluids (e. g. Wooding, 1959, and Brigham et al., 1961). For the immiscible fluids water displacing air during ordinary infiltration at the soil surface, the same principles apply for the potential development of fingers of water moving ahead of the average wetting front into the unsaturated soil profile. For miscible fluids, the thickness of the interface region is not constant and tends to increases owing to molecular diffusion. Hence, with the viscosity and density of the interfacial fluid being neither those of the displacing nor displaced fluid and with the pore geometry only implicitly considered through the value of K_p , (9.34) holds only approximately for soils.

9.4.4 Influences of Solution Concentration and pH

Recalling from section 9.1.2, the surface charge characteristics of soil particles and colloids are of two general types - one having a constant surface charge and a variable surface potential, and the other having a constant surface potential and a variable surface charge (Bolt, 1979).

The interplay of these chemical effects on transport during the displacement of pulses of solution containing ${}^{36}Cl^{-}$ through a water-saturated Oxisol (Nkedi-Kizza, 1979) is shown in Fig. 9.18. In Fig. 9.18a, as the concentration of the soil solution decreases from 0.1 to 0.001 N CaCl₂, the ${}^{36}Cl^{-}$ elution curves shift to the right with their maxima decreasing. At a pH of 4, Cl⁻ is adsorbed. Owing to the fact that an equal number of negative and positive exchange sites exists at pH 3.6 for this soil, we expect ${}^{36}Cl^{-}$ to be exchanged for their non radioactive isotopes on the clay surfaces. Differences in shapes and positions of the curves in Fig. 9.18a are a result of the concentration of the soil solution rather than caused by hydrodynamic and geometric aspects of the flow regime.

As the pH of the soil increases above 3.6, the relative proportion of negative to positive exchange sites increases. Thus, as shown in Fig. 9.18b for a constant soil solution concentration of 0.001 N, the ${}^{36}Cl^{-}$ elution curve shifts to the left as the pH increases. At pH 9, the early arrival of ${}^{36}Cl^{-}$ is indicative of a solute that is repelled from the predominantly negatively charged clay surfaces.



Figure 9.18. Breakthrough curves for a water-saturated, Ca-saturated Oxisol. a. ³⁶Cl in a CaCl₂ solution displacing a solution of an identical chemical composition for three different concentrations at a pH of 4. b. ³⁶Cl in a 0.001 N CaCl₂ displacing a solution of an identical chemical composition for three different values of pH.

Although arid soils usually are dominated by constant charge colloids and tropical soils by those of constant potential, all soils are mixtures of both, and hence their behavior under conditions that induce shifts in pH cannot be ignored.

9.4.5 Influence of Displacement Length

The mixing and attenuation of a solute by convection depend upon the pore size distribution and the number of bifurcations experienced by the soil solution as water flows through its system of microscopic pores (recall Fig. 9.6). The greater the total macroscopic displacement length, the greater will be the



Figure 9.19. Chloride and tritium breakthrough curves for 30, 90 and 120 cm long, water-saturated sandstone columns.

opportunity for both convective and diffusive mixing. As the displacement length increases, both the number of bifurcations in the pore system and the time for molecular diffusion increase.

Corey et al. (1963) examined such a displacement as well as the nature of the pore structure of a uniform, consolidated sandstone by using five column lengths. Breakthrough curves for 75-ml pulses of tritiated CaCl₂ solution (Fig. 9.19) displaced through three of the columns illustrate the progressive attenuation of the initial concentration C_o as the solute is displaced through greater macroscopic lengths. Having traveled 150 cm, the relative concentration was reduced to about 0.4. A practical implication of such attenuation is the dilution of a solute within a soil profile without leaching any of its total mass beyond a desired depth.

Note in Fig. 9.19 that the chloride appears earlier in the effluent than the tritium and the separation between the data increases with column length. This behavior demonstrates the differences of the interactions between each of the solutes and the sandstone matrix. By conducting displacement experiments with homogeneous columns of different lengths, the relative amounts of convective and molecular diffusive mixing can also be ascertained when a series of different average pore water velocities are employed. Corey et al. avoided the difficulty of packing long soil columns with sufficent uniformity by using a naturally occurring homogeneous sandstone.

9.5 Theoretical descriptions

9.5 THEORETICAL DESCRIPTIONS

With soil physicists continuing their propensity to focus on geometric considerations, soil chemists focusing on chemical reactions and ignoring geometric effects and soil microbiologists and plant nutritionists limiting their investigations to biotic absorption, our understanding of the leaching process in soil profiles remains incomplete. This deficiency reflects our present-day inability to integrate simultaneously the most relevant physical, chemical and biological processes in a unified theoretical framework. Only recently have there been attempts to model transport in multicomponent systems with consideration of microbial activity and chemical reactions (e.g. Yeh and Tripathi, 1991, Richter et al., 1992, and Šimunek and Suarez, 1994). Several theoretical opportunities provide a basis for future experiments and analyses.

9.5.1 The Convective-Diffusion Equation

 $S = \rho_T C_S + \theta C + (P - \theta) C_G$

Here we derive the cornerstone of most theoretical descriptions of solute transport in porous media recognizing its form is tentative in several aspects besides being fraught with uncertainties of applicable temporal (Skopp, 1986) and spatial scales (Dagan, 1986) that are not easily resolved.

We begin with the prism element having edges of length Δx , Δy and Δz given previously in Chapter 5 (Fig. 5.14). The difference between the mass of solute entering the prism and that leaving the prism equals the difference of the solute stored in the prism in time Δt providing that we account for any appearance (source) or disappearance (sink) of the solute within the prism by mechanisms other than transport. Hence, we obtain similar to (5.62) the equation of continuity of solutes S [M L⁻³]

$$\frac{\partial S}{\partial t} = -\left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right) + \sum_i \phi_i$$
(9.35)

where J_x , J_y and J_z are the flux densities of solute in directions x, y and z and ϕ_i [ML⁻³T⁻¹] the i-th source or sink occurring within the prism usually considered irreversible during the time period over which the equation applies.

In general, soil solutes exist in both gaseous and aqueous phases as well as being associated with the solid organic and inorganic phases of the soil. Here, we neglect the fact that non aqueous polar and non polar liquids can also reside in soils and participate in the displacement process. We assume that at least some solutes in the soil solution are sufficiently volatile to consider their content or transport in the gaseous phase. Hence, the total solute concentration S in (9.35) is

(9.36)

where ρ_T is the soil bulk density [M L⁻³], C_S the solute adsorbed or exchanged on the soil solids [M (M of dry soil)⁻¹], θ the volumetric soil water content, and C the solute in solution [M L⁻³], P the porosity and C_G the solute in the soil air [M L⁻³].

The solute flux density J in (9.35) relative to the prism $\Delta x \Delta y \Delta z$ is difficult to define unambiguously owing to the fact that the representative elementary volumes of each of the terms in J and S are not necessarily equal nor known, particularly for structured field soils. Each of the directional components of J is comprised of contributions of solute movement within the gaseous and liquid phases as well as along particle surfaces of the solid phase. We assume that solute movement along soil particle surfaces is nil or can be accounted for by functions relating the concentration of solutes in solution to that associated with the solid phase in (9.36). Hence, the solute flux density consists of three terms, one describing the bulk transport of the solute moving with the flowing soil solution, the second describing the solute moving by molecular diffusion and meandering convective paths within the soil solution and the third accounting for molecular diffusion in the gaseous phase. For the z-direction, we have

$$J_{z} = q_{z}C - \theta \left(D_{c_{z}} + D_{m_{z}} \right) \frac{\partial C}{\partial z} - (P - \theta) D_{G} \frac{\partial C_{G}}{\partial z}$$
(9.37)

where q_z is the Darcian flux, D_{c_i} and D_{m_i} are the coefficients of convective dispersion and molecular diffusion in the soil solution, respectively, D_G the molecular diffusion coefficient in the soil air and C_G the gaseous solute concentration in the soil air. Equations for J_x and J_y are identical to (9.37) when z has been replaced by x and y, respectively. We continue the analysis here for only the vertical soil profile direction z avoiding vectorial and tensorial notation.

Substituting (9.36) and (9.37) into (9.35), we obtain for a solute of the soil solution that does not volatilize into the soil air

$$\frac{\partial(\rho_T C_S)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z} \left[\theta \left(D_c + D_m \right) \frac{\partial C}{\partial z} \right] - \frac{\partial(qC)}{\partial z} + \sum_i \phi_i \,. \tag{9.38}$$

The first term of (9.38) describes the rate at which a solute reacts or exchanges with the soil solids. Its exact form (Helfferich, 1962) continues to be debated. We discuss both equilibrium and kinetic rate terms commonly used to describe this adsorption-exchange process in the next section.

With
$$D_a = (D_c + D_m)$$
, (9.38) reduces to

$$\frac{\partial(\rho_T C_S)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_a \frac{\partial C}{\partial z} \right) - \frac{\partial(qC)}{\partial z} + \sum_i \phi_i.$$
(9.39)

Although the source-sink term ϕ_i in (9.38) or (9.39) has most often been considered in the absence of the rest of the equation in many disciplines, it is often approximated by zero- or first-order rate terms

$$\phi_i = \gamma \theta + \gamma_s \rho + \mu \theta C + \mu_s \rho_T C_s \tag{9.40}$$

where γ and γ_s are rate constants for zero-order decay or production in the soil solution and solid phases, respectively, and μ and μ_s are similar first-order rate constants for the two phases. For radioactive decay, physicists may safely assume that μ and μ_s are identical as well as assuming that both γ and γ_s are nil. Microbiologists, considering organic and inorganic transformations of soil solutes in relation to growth, maintenance and waste metabolism of soil microbes as a Michaelis-Menten process, often simplify their considerations to

that of ϕ_i in (9.40). McLaren (1970) provided incentives to study such reactions as functions of both space and time in soil systems - a task not yet achieved by soil microbiologists, especially when the individual characteristics of each microbial species is quantified and not lumped together as a parameter of the entire microbial community. Agronomic or plant scientists consider ϕ_i as an irreversible sink and source of solutes taking place in the vicinity of the rhizosphere of cultivated or uncultivated plants as a function of soil depth and time as well as some empirical function defining the root distribution.

For a solute that does not appreciably react with the soil particles, does not exist in the soil air and does not appear or disappear in sources or sinks, respectively, (9.39) reduces to

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(D_a \frac{\partial C}{\partial z} \right) - \frac{\partial (vC)}{\partial z}$$
(9.41)

which is identical to (9.27) of Bachmat and Bear. For steady state flow in a homogeneous soil at constant water content, (9.41) reduces still further to

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z}$$
(9.42)

which has been extensively used to develop empirical relations between the apparent diffusion coefficient D_a and the average pore water velocity v.

An intensively measured, field scale miscible displacement experiment conducted to ascertain the distributions of D_a and v was reported by Biggar and Nielsen (1976). During steady state water flow conditions, they measured the leaching of water soluble salts at six soil depths to 1.8 m within 20 subplots of a 150-ha field. For times $0 < t \le t_1$ the soil was leached steadily with water having a concentration C_o (chloride or nitrate). For times t < 0 and $t > t_1$ the soil was leached with water having a concentration C_i . In view of the large pore water velocities measured in their experiment, the appropriate initial and boundary conditions for the solution of (9.42) were

$C = C_i$	z>0	t=0	
$C = C_o$	z = 0	$0 < t \leq t_1$	(9.43)
C=C	z=0	$t > t_1$	

The measured concentration C(z, t) was fitted to the solution of (9.42) subject to (9.43)

$$\frac{C-C_i}{C_o-C_i} = \frac{1}{2} \left\{ erfc \left[\frac{z-vt}{\left(4D_a t\right)^{1/2}} \right] + \exp\left(\frac{vz}{D_a}\right) erfc \left[\frac{z+vt}{\left(4D_a t\right)^{1/2}} \right] \right\} - \frac{1}{2} \left\{ erfc \left[\frac{z-v(t-t_1)}{\left[4D_a(t-t_1)\right]^{1/2}} \right] + \exp\left(\frac{vz}{D_a}\right) erfc \left[\frac{z+v(t-t_1)}{\left[4D_a(t-t_1)\right]^{1/2}} \right] \right\}^{(9.44)}$$

at different locations within the field to obtain 359 values of (D_a, v) which are plotted against each other in Fig. 9.20. Values of D_a were logarithmically normally distributed with a mode of 4.0, a median of 85.1 and a mean of 367.6 cm²·d⁻¹. Values of v were also logarithmically normally distributed having a mode of 4.3, a median of 20.3 and a mean of 44.2 cm·d⁻¹ (see Fig. 9.25). The solid

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10⁵ а (cm²·10³) Q^{* 10¹} 10.1 10⁰ 10¹ 10² 10³ 10-1 $v (cm \cdot d^{-1})$ 10⁵ b Biggar and Nielsen (1976) 10³ 0^{*}0 10¹ Pfannkuch (1963) 10-1 10-6 10-4 10-2 100 10² vdD_{o}^{-1}

Figure 9.20. a. Field-measured values of the apparent diffusion coefficient D_a plotted against average pore water velocity v. b. Values of $D_a D_o^{-1}$ plotted against Peclet number vdD_o^{-1} where D_o is the molecular diffusion coefficient and d is the mean soil particle diameter.

line in Fig. 9.20a obtained by regressing $\ln(D_a - 0.6)$ versus $\ln v$ is of the same form as (9.31). The value of 0.6 represents the molecular diffusion coefficient for the unsaturated soil taking into account the average tortuosity and the average soil water content during displacement. The same data plotted as $D_a D_o^{-1}$ versus vdD_o^{-1} (Peclet number) in Fig. 9.20b where *d* is the mean soil particle diameter can be compared to those reported by Pfannkuch (1962) measured by several investigators in the laboratory using homogeneously packed columns. With the value of the coefficient $\beta = 2.93$ being two orders of magnitude greater that found in the majority of laboratory column studies, the impact of soil structure and the large range of particle diameters and pore sizes on the dispersion of solutes in natural field soils is abundantly evident. 9.5.1.1 Solutes in Continual Equilibrium with the Solid Phase

Instantaneous adsorption or exchange reactions included in the first term of (9.38) are described by equilibrium isotherms $C_s(C)$ of several different forms - mass action, linear, Freundlich, Langmuir or other functional forms (van Genuchten et al., 1974; Bolt, 1979; and Travis and Etnier, 1981).

The most common approach for modeling the first term of (9.38) has been to assume instantaneous adsorption or exchange as well as simple linearity between C_s and C [$C_s = kC$ where k is the slope of the isotherm $C_s(C)$ often referred to as the distribution coefficient K_d]. If we put this linear isotherm in (9.39) we have

$$\frac{\partial(\rho_T kC)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_a \frac{\partial C}{\partial z}\right) - \frac{\partial(qC)}{\partial z} + \sum_i \phi_i$$
(9.45)

which reduces to

$$R\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} + \sum_i \phi_i \, \theta^{-1}$$
(9.46)

for steady state flow in a homogeneous soil and where R is a retardation factor $(= 1 + \rho_T k \theta^{-1})$. Equation (9.46) has been solved for many conditions for both finite and semi-infinite systems (van Genuchten and Alves, 1982; Javandel et al., 1984). While the simplicity of a linear isotherm is a convenient feature for mathematically modeling, its limitations are clearly apparent owing to adsorption and exchange processes usually being nonlinear and depending upon the competing species in the soil solution (see Reardon, 1981; Miller and Benson, 1983; and Valocchi, 1984).

9.5.1.2 Solutes Not in Equilibrium with the Solid Phase

Diffusion-controlled or chemically controlled kinetic rate reactions included in the first term of (9.38) have been described in a variety of equations. We consider here three of the more popular formulations.

The most simplest formulation is that of a first order linear kinetic reaction where (9.39) is replaced by two coupled equations. Here, for steady state flow through a homogeneous soil without sources or sinks, we have

$$\frac{\rho_T}{\theta} \frac{\partial C_s}{\partial t} + \frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z}$$

$$\frac{\partial C_s}{\partial t} = \alpha (kC - C_s)$$
(9.47)

where α is a first order rate constant. The success of this and similar rate models (e. g. Davidson and McDougal, 1973; van Genuchten et al., 1974) has been best when miscible displacement experiments have been carried out at relatively slow velocities when mixing is dominated by molecular diffusion. Nevertheless, under such conditions the values of α and k may indeed be biased owing to the use of an average value of v which does not embrace the spatial distribution of the solute influencing the rate reaction within soil pores at the microscopic scale. The second formulation gives more consideration to the microscopic pore water velocity by defining a bimodal distribution which partitions the soil water into mobile and immobile phases. In the mobile phase where soil water flows, solute behavior is described by a convective-diffusion equation. Inasmuch as water is stagnant in the immobile phase, solutes move in and out of this phase only by molecular diffusion. Zones of stagnant water derive from thin liquid films around soil particles, dead-end pores, non moving intraaggregate water or isolated regions associated with unsaturated conditions. Miscible displacement equations based on first order exchange of solute between mobile and immobile phases initially discussed by Coats and Smith (1964) were extended by van Genuchten and Wierenga (1976) to include Freundlich type equilibrium adsorption-desorption processes. Their equations are

$$\theta_m R_m \frac{\partial C_m}{\partial t} + \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_{a_m} \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z}$$

$$\theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im})$$
(9.48)

where the subscripts m and im refer to the mobile and immobile phases, respectively. The retardation factors account for equilibrium type adsorption processes similar to that in (9.46) while the mass transfer coefficient α embraces a diffusion coefficient and an average diffusional path length. Although (9.48) was used successfully by van Genuchten and Wierenga and by Gaudet et al. (1977) as well as many others more recently to describe laboratory column studies, its use in structured field soils has been limited owing to the difficulty of obtaining reliable values of α which depend upon the geometry of the soil pore structure (van Genuchten, 1985). For laboratory experiments, the value of α may well be confounded with nonlinear isotherm and chemically kinetic exchange effects. Moreover, the fraction of θ considered to be immobile is sensitive to hysteresis, the concentration of the soil solution, the soil water content and the soil water flux. From the experimental studies of Nkedi-Kizza mentioned earlier in section 9.4.1.4, Fig. 9.21 clearly shows the impact of the solution concentration and the average pore water velocity on the amount of soil water considered to be immobile.

The third formulation considers the first term of (9.38) having two components - one for exchange sites (type 1) on a fraction of the soil particle surfaces that involve instantaneous, equilibrium reactions and another for type 2 exchange sites involving first order kinetics or those assumed to be timedependent (Selim et al., 1976; Cameron and Klute, 1977). Following Nkedi-Kizza et al. (1984) we have

 $(1+F\rho_T k \theta^{-1}) \frac{\partial C}{\partial t} + \rho_T \theta^{-1} \frac{\partial C_{s_1}}{\partial t} = D_a \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z}$ $\frac{\partial C_{s_2}}{\partial t} = \alpha [(1-F)kC - C_{s_2}]$ (9.49)

where F is the mass fraction of all sites being occupied with type 1 sites, and where subscript 2 refers to type 2 sites. With values of α and F usually being dependent upon the average displacement velocity v, values of F appropriate for (9.49) cannot be obtained from equilibrium batch studies. The use of an





average value of v masks any effect of the microscopic pore water velocity distribution on the exchange process.

Comparison of (9.48) and (9.49) shows that they can be put in the same dimensionless form by means of equation-specific dimensionless parameters. With this information Nkedi-Kizza et al. (1984) proved that effluent curves from laboratory soil columns alone cannot be used to differentiate between the specific physical and chemical phenomena that cause an apparent non equilibrium situation during miscible displacement. The similarity of the two sets of equations allows an oftentimes satisfactory empirical description of the mixing of solutes at the macroscopic scale by either equation without ascertaining the exact nature of the particular chemical or physical process at the microscopic scale. The exact nature of the processes awaits further research using micro tomography or other techniques of observation at the microscopic scale.

9.5.1.3 Dual-Porosity Models for Structured Soils

Dual porosity models (also called bi-modal porosity models) assume that a soil can be separated into two distinct pore systems superpositioned over the same

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by

soil volume with each system being a homogeneous medium having its own water and solute transport properties (Dykhuizen, 1987). We assume that the same type of mathematical expressions can be used to describe both systems of pores inasmuch as similar capillary effects take place in the pores of both systems (Othmer et al., 1991). With the two systems exchanging water and solutes in response to hydraulic and concentration gradients, the soil is characterized by two water velocities, two hydraulic heads, two water contents and two solute concentrations. Gerke and van Genuchten (1993) provide a comprehensive review of various theoretical and experimental attempts to deal with water and solute movement in saturated and unsaturated structured soils during steady and transient water flow conditions. The basis of their numerical simulations demonstrating the complicated nature of solute leaching in structured, unsaturated soils during transient water flow are summarized here to provide future opportunities for field research in soil hydrology.



Figure 9.22. Schematic diagram of a structured soil at the microscopic level. Macropores, interaggregate pores and fracture pores appear between shaded areas representing soil aggregates. Arrows represent water and solute movement through a. the surface of an aggregate, through b. the fracture pore, between c. aggregates, between d. continuous and stagnant pores and inside e. an aggregate.

Microscopically, a structured soil (see Fig. 9.22 and our discussion in sections 2.4, 4.3.3 and 5.3.2) consists of soil aggregates (shaded irregular areas) surrounded by inter-aggregate pores (dotted areas) which form a more or less continuous network. The pore network is geometrically a combination of inter-aggregate and intra-aggregate pores further complicated by the presence of distinct mineral and organic particles discussed earlier. Here we use subscript M to denote the inter-aggregate system and subscript m to denote the intra-

aggregate system. We refer the reader to the original article of Gerke and van Genuchten (1993) for a complete description of the hydraulic properties of the structured soil and the details of the solute transport equations only briefly described here.

Solute transport with linear adsorption and first order decay is described

$$\frac{\partial(\theta_M R_M C_M)}{\partial t} = \frac{\partial}{\partial z} \left(\theta_M D_{a_M} \frac{\partial C_M}{\partial z} - q_M C_M \right) - \theta_M \mu_M C_M - \frac{\Gamma_s}{w_M}$$
(9.50)
$$\frac{\partial(\theta_m R_m C_m)}{\partial t} = \frac{\partial}{\partial z} \left(\theta_m D_{a_m} \frac{\partial C_m}{\partial z} - q_m C_m \right) - \theta_m \mu_m C_m + \frac{\Gamma_s}{1 - w_M}$$
(9.50)

where μ is a first order decay coefficient, Γ_s a solute mass transfer term to which both molecular diffusion and convective transport contributes and w_M is the ratio of the volume of the interaggregate pores to that of the total volume of all pores. With the exception of Γ_s which is defined as the mass of solutes per unit volume of bulk soil per unit time, all variables in (9.50) are defined relative to the partial volume of each pore system.

Although this model and its numerical solution can simulate transport related to specific chemical and physical properties of the soil, its large number of parameters not easily measured experimentally remain a topic of future laboratory and field research.

9.5.1.4 Consecutive Convective-Diffusion Equations

Equation (9.39) is oftentimes sequentially repeated when organic or inorganic products are of interest, especially when the products form a consecutive chain of reactions, e. g. for nitrogen (urea \rightarrow NH₄⁺ \rightarrow NO₃⁻ \rightarrow N₂). In such cases a set of simultaneous equations stemming from (9.39) becomes

$$\frac{\partial(\rho_{T}C_{S_{1}})}{\partial t} + \frac{\partial(\theta C_{1})}{\partial t} = \frac{\partial}{\partial z} \left(D_{a_{1}} \frac{\partial C_{1}}{\partial z} \right) - \frac{\partial(qC_{1})}{\partial z} + \phi_{1}$$

$$\frac{\partial(\rho_{T}C_{S_{j}})}{\partial t} + \frac{\partial(\theta C_{j})}{\partial t} = \frac{\partial}{\partial z} \left(D_{a_{j}} \frac{\partial C_{j}}{\partial z} \right) - \frac{\partial(qC_{j})}{\partial z} - \phi_{j-1} + \phi_{j}$$
(9.51)

where $j = 2, 3, \dots n$ when n is the number of species considered in the reaction chain. The equations are linked to each other by their mutual ϕ_j terms. These equations have been applied to consecutive decay reactions of soil nitrogen species (e. g. Cho, 1971; Misra et al., 1974; Starr et al., 1974), organic phosphates (Castro and Rolston, 1977) and pesticides (Bromilow and Leistra, 1980).

We illustrate the application of (9.51) with an investigation conducted by Wagenet et al. (1977) who extended the mathematical analysis of Cho (1971) and the experimental techniques of Mansell et al. (1968) and Misra et al. (1974) to trace the fate of nitrogen applied as a pulse of 95% ¹⁵N-enriched urea fertilizer to an unsaturated soil column during steady state leaching conditions. The concentration of oxygen within the partially air-filled pores was simultaneously controlled at a desired constant value (Wagenet and Starr, 1977). The transport

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Figure 9.23. Concentration distributions of different nitrogen species identified in the effluent and soil from a pulse of ¹⁵N-enriched urea solution displaced through a column under controlled laboratory conditions.

and transformation of urea, NH_4^+ and NO_3^- were identified by isotopic dilution techniques. Based upon complementary experiments, the enzymatic hydrolysis of urea C_1 , the microbial oxidation of ammonium C_2 and the microbial reduction of nitrate C_3 were each considered first order rate reactions. For their study, (9.51) become

$$(1+R_1)\frac{\partial C_1}{\partial t} = D_a \frac{\partial^2 C_1}{\partial z^2} - v \frac{\partial C_1}{\partial z} - k_1 C_1$$

$$(1+R_2)\frac{\partial C_2}{\partial t} = D_a \frac{\partial^2 C_2}{\partial z^2} - v \frac{\partial C_2}{\partial z} + k_1 C_1 - k_2 C_2$$

$$\frac{\partial C_3}{\partial t} = D_a \frac{\partial^2 C_3}{\partial z^2} - v \frac{\partial C_3}{\partial z} + k_2 C_2 - k_3 C_3$$
(9.52)

where R_1 and R_2 are the retardation factors for urea and ammonium [see (9.46)], respectively, D_a assumed to be identical for each of the chemical species and k_1 , k_2 and k_3 are the rate constants describing the processes of urea hydrolysis, ammonium oxidation and nitrate reduction, respectively.

Elution curves for the three chemical species identified by the ¹⁵N tracer introduced as a 100-ml pulse of urea solution ($C_1^o = 1000 \text{ mg} \cdot 1^{-1}$) into a soil column having 20% oxygen in its air-filled pores are shown in Fig. 9.23a. Theoretical and measured concentrations of NH₄⁺-N and NO₃⁻-N in the soil solution and those of adsorbed NH₄⁺-N in the soil column at the conclusion of the displacement process (t = 186 h) are given in Fig. 9.23b and c, respectively. Details of the methodology to ascertain values of v, D_a , R_1 , R_2 , k_1 , k_2 and k_3 used in the solutions of (9.5) subject to appropriate initial and boundary conditions are given by Wagenet et al. The rate of nitrification in the presence of 20% oxygen was one order of magnitude greater than that of denitrification. Of the 100 mg ¹⁵N applied to the soil, a mass balance of the ¹⁵N in the chemical species measured in the effluent and in the soil at the conclusion of the experiment was within less than 3 mg.

With consecutive equations such as (9.52), field studies in the presence of higher plants provide opportunities to better understand agro-ecosystems. For example, Mishra and Misra (1993) learned how liming a cultivated field of corn modified the values of k_2 and k_3 as a function of soil depth and time in the presence and absence of crop roots. A better understanding of microbial-induced transformations of other chemical species for transient flow and nonisothermal conditions await investigation in both the laboratory and the field.

9.5.2 Chromatographic Formulations

Descriptions of the transport of fluids with their dissolved constituents through beds of reactive porous solids based upon chromatographic plate formulations stem primarily from those derived by chemical engineers nearly one-half century ago (e.g. Wilson, 1940; DeVault, 1943; Thomas, 1944, Glueckauf, 1949; Lapidus and Amundson, 1952; and Heister and Vermeulen, 1952). Subsequent studies in soil hydrology focused first on laboratory soil columns and later were applied in the field for reclaiming saline and sodic soils. For example, to describe cation exchange and ionic distributions within soil columns, Rible and Davis (1955) used DeVault's theory while Bower et al. (1957) used that of Heister and Vermeulen. Van der Molen (1956) predicted the reclamation of saline soils during winter rainfall periods using the theory of Glueckauf. Dutt and Tanji (1962) introduced computer-based chromatographic formulations that were

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followed by those of Kovda and Szabolcs (1979) and Oster and Frenkel (1980) which were applied to soil reclamation. Shaffer (1977) extended the model of Dutt to apply to cropped, tile-drained field soils.





The chromatographic formulation introduced by Dutt and Tanji (1962) is illustrated in Fig. 9.24 where a vertical, homogeneous soil column of length L of unit cross-sectional area is made up of n segments (plates) each of length Δz_i . The concentration C_j of a number of solute species j entering the column in each leaching aliquot ΔQ_m (where m is the number of the aliquot) changes as the solutes mix, react and pass through each segment. The first aliquot infiltrates into the first segment, and fills it to some prescribed soil water content. The second aliquot of infiltrating water displaces the soil water from the first segment into the second segment, and so forth. If the amount of solution ΔQ in each segment Δz_i is identical during infiltration, the final concentration C_j^* of solute species j in the first aliquot ΔQ_1 leached from the column will be

 $C_j^* = C_j + \sum_{i=1}^n \Delta C_{ij}$

where ΔC_{ii} is the change in concentration of solute *i* when the aliguot ΔO_1 is passed through segment Δz_i . As $n \to \infty$, the last term in (9.53) is the integral of the change in solute concentration from z = 0 to z = L. Assuming that the solution is in chemical equilibrium with the soil in each segment, the difference in concentration between the equilibrium solution and that entering each segment is calculated. If n in (9.53) is considered finite, the average concentration of the aliquots ΔQ_m is calculated by progressively equilibrating the solution of ΔQ_m with each of the *n* segments assuming that piston flow (Fig. 9.12a) takes place within each segment. The dispersion of the solutes associated with pore water velocity distributions and molecular diffusion are implicitly and empirically included by choosing the number of segments or plates n. Tanji et al. (1972) utilized the concept of holdback H_b [see (9.33)] to allow only a fraction of the soil water in each segment to be displaced into the next after chemical equilibrium. They also designated variable segment thicknesses Δz_i corresponding to soil sampling depth intervals or soil horizons as well as choosing the value of n based upon the dispersion of measured chloride breakthrough curves.

Because transient perturbations of the pore water velocity distribution and soil water content are ignored during infiltration and redistribution, chromatographic formulations of solute transport have more recently emphasized the need to study the kinetic aspects of chemical reactions, exchange processes and dissolution and precipitation. Even when these kinetic aspects have been articulated, the enigma of choosing the number and thickness of the segments to reconcile the omission of the pore water velocity distribution remains the objective of future research.

9.5.3 Stochastic Considerations

Because of the naturally occurring heterogeneity of field soils, deterministic formulations of solute transport processes presented above generally must be modified to describe pedon or field scale solute transport. Contemporary research efforts are based upon the consideration that transport phenomena are intrinsically erratic processes susceptible to quantitative characterization by stochastic models. Common to all stochastic models of pedon or field scale transport is the assumption that parameters observed in the field are functions with values distributed in space represented as random variables with discrete values assigned according to a probability distribution. The probability distribution functions at each point in space are usually unknown and cannot be evaluated from only one or a few observations within close proximity of the location. Reviews by Jury (1983) and Dagan (1986) provide pedagogic details. Many other statistical approaches are also described in the literature [e.g. continuous Markov processes (Knighton and Wagenet, 1987), random walk formulations (Kinzelbach, 1988), moment analyses (Cvetkovič, 1991) and hierarchical methods (Wheatcraft and Cushman, 1991). Here, we consider three approaches that are available to deal with spatial and temporal variability in addition to the state-space equations previously described in Chapters 7 and 8.

9.5.3.1 Monte Carlo Simulations

Monte Carlo simulations of a solution of a deterministic equation such as (9.42) allow coefficients to be random variables of the nature expected within a heterogeneous field soil. The variable may be independent, spatially or temporally correlated and perhaps manifest a variance structure. Based upon an initial sampling, parameters selected for the assumed probability density function (pdf) permit repeated solutions ($i = 1, 2, \cdots$) of the deterministic equation [e.g. $C_i(z, t)$] to be calculated. These solutions $C_i(z, t)$ are then used to calculate sample moments (mean, variance) which are assumed to represent the statistical properties of the underlying stochastic process.



Figure 9.25. Probability distribution functions of D_a and v presented in Fig. 9.20.



Figure 9.26. Solute concentration distributions within a field soil. a. Monte Carlo simulation and b. Deterministic equation (9.44). Measured values and their standard deviations are represented by solid circles and horizontal bars, respectively.

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Amoozegar et al. (1982) relied on the initially measured observations of D_a and v shown in Fig. 9.20a and their pdfs shown in Fig. 9.25 together with the normal pdf of θ to estimate the solute concentration distribution $C(z, t)/C_o$ expected at any location within a field. The average solute concentration distribution $\overline{C}(z,t)/C_o$ expected for the entire field was derived from repeated calculations of (9.44) using the following Monte Carlo step-wise procedure:

1. Draw a random value from the normal distribution with mean zero and standard deviation 1 (Maisel and Gnugnoli, 1972).

2. Find random values of $\ln D$, $\ln v$ and/or θ from their respective statistical distributions represented by the equation $y = \beta \sigma + \mu$ where β is the value with mean zero and standard deviation 1, and y is the random value with mean μ and standard deviation σ .

3. Calculate the random value of C/C_o from (9.44) using the above values of D_a , v and θ for each z and t.

4. Repeat steps 1 through 3 above 2000 times and calculate the mean value of C/C_0 for each z and t..

The average solute concentration distribution $\overline{C}(z,t)/C_o$ expected for the entire field at time t = 2 d for a pulse input of solute concentration C_o for $t_1 = 0.4$ d is shown in Fig. 9.26a together with the field values measured by Biggar and Nielsen (1976). Note that these distributions differ markedly from those in Fig. 9.26b calculated from (9.44) using constant values of D_a , v and θ . The spreading of the solute averaged over the entire field is dominated by variations in pore water velocity (Bresler and Dagan, 1979, and Dagan and Bresler, 1979).

Two kinds of solute distributions are of interest. The first kind is that of $C(z, t)/C_o$ realized at any location within a field, and the second is that of $\overline{C}(z,t)/C_o$ obtained by averaging a large number of $C_i(z, t)/C_o$ across a field. The former is important because it is associated with a particular soil pedon location, a single crop plant or a small community of plants. With site-specific crop and soil management practices, each location can indeed be treated and managed individually across the entire field in order to account for local variations of soil properties (Robert et al., 1993). The latter is important because it is the expectation of solute retention and emission of solutes from an entire field considered as a single domain. Although there is general appreciation of the latter, a farmer is also appreciative of the former owing to the desire to provide optimum growing conditions for each and every crop plant within the cultivated field.

Present-day research within soil mapping units focusing on auto- and cross-correlation lengths of soil properties and variables [such as those in (9.44)] will eventually allow the delineation of the extent of a field characterized by a single simulation. The opportunities afforded by Monte Carlo simulations hinge upon the development of methods to measure and ascertain pdfs of the transport coefficients within prescribed limits of vadose zone depths and times.

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9.5.3.2 Stochastic Continuum Equations

Recognizing the paucity of solute concentration data usually available in soils and other subsurface environments coupled with their natural geometric complexities and heterogeneity, Gelhar et al. (1979) initiated stochastic continuum formulations to describe transport processes in water-saturated aquifers. Unlike the above Monte Carlo methods which assume that the random parameters or variables have no spatial correlation, stochastic continuum formulations assume that a random variable can be represented by the sum of its mean and a spatially correlated random fluctuation.

We illustrate the approach with Darcy's equation that describes the mean vertical water flux density \bar{q} in a saturated soil (5.5) as

$$\overline{q} = -\overline{K}_{S} \frac{d\overline{H}}{dz}.$$
(9.54)

where , \overline{q} , \overline{K}_{S} and \overline{H} are expected mean values. Assuming that the values of z and its derivative are measurable and known deterministically within desired, prescribed limits of accuracy, (9.54) can be written as

$$q = (\overline{q} + \widetilde{q}) = -\left(\overline{K}_{S} + \widetilde{K}_{S}\right) \frac{d(\overline{H} + \widetilde{H})}{dz}$$
(9.55)

where each of the terms \tilde{q} , \tilde{K}_{S} and \tilde{H} are random, spatially autocorrelated functions and have a zero mean value. Subtracting (9.54) from (9.55) yields

$$\bar{q} = -\bar{K}_S \frac{d\bar{H}}{dz} - \bar{K}_S \frac{d\bar{H}}{dz} - \bar{K}_S \frac{d\bar{H}}{dz}.$$
(9.56)

The terms in such an equation evaluated by deriving a first-order equation for the fluctuations are solved with Fourier transforms (Gelhar et al., 1979).

When a random parameter such as D_a in (9.42) is represented by the sum of its mean value and a random fluctuation, a mean transport model with additional terms is obtained. By solving the stochastic equation of the local-scale water and solute transport, the functional form of D_a for macroregions is related to the statistics describing the variability. A macro-scale value of D_a is reached asymptotically as distance and/or time increase. From such an analysis the longterm, large-scale solute transport can be described using the stochastically derived value of D_a in the deterministic equation (9.42).

A limited number of field aquifer experiments (e.g. Sudicky et al. 1985, and Freyberg, 1986) have shown that the value of D_a increases with solute travel time and travel distance and gradually approaches a constant asymptote consistent with the analysis proposed by Gelhar et al. The application of stochastic continuum research for unsaturated soils appears promising (e.g. Russo, 1993, and Yeh et al., 1985a, b and c) but not yet sufficiently developed to be a proven field technology.

9.5.3.3 Stochastic Convective Equations

The displacement and attenuation of a solute distribution within a vertical soil profile during infiltration can be considered the result of a stochastic convective flow process with its formulation based upon a solute travel time probability density function. The advantage of such formulations is that they do not require an explicit accounting of all of the various physical, chemical and biological processes occurring in the complex, heterogeneous soil environment. Although many stochastic convective models have been used in different scientific disciplines, those initiated by Simmons (1982) and Jury (1982) stimulated research in soil hydrology during the past decade. Here we introduce the stochastic convective concept as a transfer function (Jury, 1982) which can easily be obtained for a nonreactive solute by a single, simple field calibration to measure the travel time distribution. It is assumed that no dispersion of the solute takes place other than that which is represented by the travel time variations within the soil.

Assuming that the depth reached by a solute applied in water at the soil surface depends upon the net amount of water applied, the probability that the solute will reach depth L after a net amount of water I has been applied to the soil surface is

$$P_{L}(I) = \int_{0}^{I} f_{L}(I') dI'$$
(9.57)

where $f_L(I)$ is the probability density function. $f_L(I)$ is the average concentration at soil depth z = L in response to a narrow pulse (Dirac δ -function) of solute C_{IN} $= C_o \delta(I)$ applied at I = 0 at the soil surface. A set of observations of $f_L(I)$ can be obtained by measuring the soil solution concentration at depth L at various locations within a field to determine the amount of uniformly applied water Irequired to move the solute pulse from the soil surface to depth L. The average concentration $C_L(I)$ at z = L for arbitrary variations of solute C_{IN} applied at the soil surface is

$$C_L(I) = \int_0^\infty C_{IN}(I - I') F_L(I') dI'.$$
(9.58)

The integrand is the probability $f_L(I')$ of reaching z = L between I' and (I' + dI'), and multiplied by the concentration $C_{IN}(I - I')$ of solution displacing at I'. For spatially variable water application rates Jury used a joint probability function in (9.58).

We assume that the distribution of physical processes contributing to the probability density $f_L(I)$ between z = 0 and z = L is the same for all soil depths. Hence the probability that an applied solute will reach any depth z after an amount of water $I = I_1$ has infiltrated the soil surface is equal to the probability of reaching z = L after $I = I_1 L z^{-1}$ has infiltrated. For example, the probability of reaching a depth of 50 cm with 10 cm of infiltrated water is equal to the probability of reaching 100 cm with 20 cm of infiltrated water. Hence, from (9.57)

$$P_{z}(I) = P_{L}\left(\frac{IL}{z}\right) = \int_{0}^{ILz^{-1}} f_{L}(I') dI'.$$
(9.59)

To predict the average solute concentration as a function of any depth $z \neq L$, we relate the probability density function $f_z(I)$ to the reference density function f_L by

$$f_z(I) = \frac{L}{z} f_L\left(\frac{IL}{z}\right)$$

/ ...

(9.60)

(9.61)

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and obtain

$$C(z,I) = \int_0^\infty C_{IN}(I-I')\frac{L}{z}f_L\left(\frac{I'L}{z}\right)dI'.$$





The concept is illustrated in Fig. 9.27 where the broken lines in the graphs for z = L and z = z represent concentration distributions measured at individual locations within the field.

If the transport properties are statistically similar for all depths, only one calibration f_L is needed. On the other hand, if they are dissimilar owing to strongly developed horizons or textural and structural differences, additional calibrations f are required or a more robust calibration f_L for all depths can be made at depth L below the strongly stratified soil.

Relatively few distributions of solute transport parameters have been measured in the field. Some of them appear to be lognormal. For such distributions the travel time density function $f_z(t)$ is

$$f_L(t) = \left[\frac{1}{(2\pi)^{1/2} \sigma t}\right] \exp\left[\frac{-(\ln t - \mu)^2}{2\sigma^2}\right]$$
(9.62)

where μ is the mean of the distribution of lnt and σ^2 the corresponding variance. On the other hand (9.44) for the same boundary and initial conditions yields the travel time density function $f_z(t)$

$$f_L(t) = \left| \frac{L}{2(\pi D_a t^3)^{1/2}} \right| \exp\left[\frac{-(L - vt)^2}{4D_a t} \right].$$
(9.63)

Although the above functions are nearly identical when calibrated at the same

depth (Simmons, 1982), they yield distinctly different predictions of solute movement at depths $z \neq L$. Jury and Sposito (1985) have shown that the variances of the travel time for (9.62) and (9.63) are

$$\operatorname{var}_{z_{\pi m}}[t] = z^2 L^{-2} \exp(2\mu) \left[\exp(2\sigma^2) - \exp(\sigma^2) \right]$$
(9.64)

and

 $\operatorname{var}_{z_{CDE}}[t] = 2Dzv^{-3},$ (9.65)

respectively. Inasmuch as $\operatorname{var}_{z_{TFM}}[t]$ increases as the square of the depth z while that of (9.44) increases linearly with depth, the lognormal transfer function model predicts the greater amount of solute spreading for the same depth. Present-day field experimentation for different soils and local conditions is sufficiently limited to preclude a preferred choice of the two models (e.g. see Jury and Sposito, 1985).

Presently, stochastic-convective formulations are being extended to include the transport of adsorbing and decaying solutes, two component chemical nonequilibrium models, physical nonequilibrium models and other nonlinear processes. See a review by Sardin et al. (1991) as well as a more recent contribution by Roth and Jury (1993).

9.6 IMPLICATIONS FOR WATER AND SOLUTE MANAGEMENT

Although our understanding and theoretical description of solute transport in soils remain incomplete, we have nevertheless sufficient knowledge to derive a few principles or guidelines for managing solute retention or leaching in the field. Whether solutes accumulate or leach depends primarily upon the processes by which they enter, react and leave the soil profile relative to their association with water. Here, we make no attempt to discuss the well-known principles of managing salinity and drainage from irrigated agricultural lands used for crop production inasmuch as excellent texts are abundantly available. Disregarding horizontal surface and subsurface water flow, we focus our attention on transport owing to the water content and flux density conditions at the soil surface occurring naturally owing to local weather conditions and being deliberately modified by irrigation.

Summarizing the more important points of this chapter, we conclude the following regarding the relative movements of soil water and its dissolved constituents:

a. As water moves more slowly through a soil, there is a greater opportunity for more complete mixing and chemical reactions to take place within the entire microscopic pore structure owing to the relative importance of molecular diffusion compared with that of convection.

b. Microscopic pore water velocity distributions manifest their greatest divergence for water-saturated soil conditions. Hence, under water-saturated conditions, the greatest proportion of water moving through the soil matrix occurs within the largest pore sequences.

c. Under water-saturated soil conditions, when the average pore water velocity is large compared with transport by molecular diffusion, the relative amount of solute being displaced depends upon the solute concentration of the invading water.

d. The concept of preferential flow paths occurs at all degrees of water-unsaturation even though their existence is usually only demonstrated for macropores near water-saturation. At each progressively smaller water content, the larger pore sequences remaining full of water establish still another set of preferential flow paths.

e. Any attempt to measure the solute concentration based on extraction methods carried out either in the laboratory or the field will be dependent upon the rate of extraction and the soil water content during the extraction process.

f. Inasmuch as rainfall infiltration usually occurs at greater soil water contents and greater average pore water velocities than does evaporation at the soil surface, the amount of solutes transported near the soil surface per unit water moving through the soil surface is greater for evaporation than for infiltration.

Each of the above six points have been verified one way or another in numerous publications before and after the observations made in a field experiment conducted by Miller et al. (1965) which we describe below.

A level 0.4-ha site of Panoche clay loam was divided into 0.004-ha plots statistically replicated in five complete blocks. Potassium chloride uniformly applied to the soil surface was leached and redistributed within the profile with four different methods of water application: a. the soil surface continuously ponded with water, b. the soil surface intermittently ponded with repeated applications of 15-cm of water, c. the soil surface intermittently ponded with repeated applications of 5-cm of water and d. the soil surface continuously sprinkled at a rate less than K_s and equal to 0.3 cm h⁻¹. The intermittent applications were made weekly when the soil water pressure head at the 30-cm soil depth reached a value of -150 cm. Each method gave rise to different soil water content distributions $\theta(z,t)$ and different water flux density distributions q(z,t). Average values $\overline{\theta(z,t)}$ and $\overline{q(z,t)}$ for each method were a. 0.48 and 0.6, b. 0.44 and 0.09, c. 0.42 and 0.03 and d. 0.42 cm³ cm⁻³ and 0.3 cm⁻¹, respectively. Soil solution samples taken every 30 cm to a depth of 150 cm were frequently extracted and analyzed in the laboratory for their chloride content. From the five plots of each treatment about 3500 samples were analyzed. Additional details regarding the exact nature of the infiltration, redistribution and soil water content profiles are available (Nielsen et al., 1967).

The chloride concentration distributions from the four water application methods manifest significant differences (Fig. 9.28). Although some chloride leached to great depths in the continuously ponded soil after 15 cm water had infiltrated, most all of the solute resided in the top 50 cm of soil. In the other three treatments for the same amount of water infiltrated, large quantities of the solute had been dispersed twice the depth to 100 cm. For 60 cm of infiltration, the center of the solute mass is displaced to greater depths as $\overline{\theta(z,t)}$ decreases.



Figure 9.28. Field-measured chloride concentration distributions from a surface application of potassium chloride being leached through the profile as a result of four different water application treatments. Values associated with each curve correspond to cumulative amounts of water infiltrated

That is, for the continuously ponded case, the relative maximum chloride concentration is just below 100 cm while those for the intermittent 5-cm ponding and for continuous sprinkling were both below 150 cm. Indeed, the concentration of solute for the latter two treatments for 60 cm of water infiltrated is everywhere less than that of the continuously ponded case when as much as 90 cm of water had infiltrated. Under the continuously ponded condition, judging the small solute concentration to a depth of 90 cm when a depth of 90 cm of water had been applied, its behavior conformed to the recommendation, "It takes a cm of water to leach a cm of soil". Here we note that for unsaturated, slow leaching conditions, it took only 60 cm of water to leach the same amount of solute as was required for 90 cm of water under nearsaturated ponded conditions. The distribution curves for intermittent 5-cm ponding and for continuous sprinkling are remarkably similar. Even though their values of q(z,t) differed by one order of magnitude, at such slow flow rates relative differences in mixing by molecular diffusion are apparently insignificant to the spreading of solute at nearly identical $\theta(z,t)$.

Two additional comments are appropriate for the data presented in Fig. 9.28. First, consider the 15-cm curve for continuous ponding, the 45-cm curve

9.6 Implications for water and solute management

for 15-cm intermittent ponding and the 30-cm curve for 5-cm intermittent ponding. If we assume that a nitrate fertilizer instead of a chloride salt had been applied to the soil surface, three entirely different solute distributions could have achieved different purposes. For continuous ponding, the fertilizer is leached in a concentrated solution for the benefit of a shallow-rooted crop. For 5-cm intermittent ponding, fertilizer is leached to the roots of a deep-rooted crop (e.g. a fruit tree crop) and not in the vicinity of an associated, shallow-rooted cover crop. The 45-cm curve for 15-cm intermittent ponding illustrates uniform fertilization to a 125-cm soil depth - a desired result for both deeper-rooted and shallow-rooted crops growing in the same community. Second, consider the curves for continuous ponding and those for 5-cm intermittent ponding. If we assume that a chlorinated pesticide moves approximately like chloride and has a lethal dose equivalent to 100 meq l⁻¹ chloride, we note that pests such as nematodes are killed to a depth greater than 100 cm if we leach the pesticide with intermittent ponding. On the other hand, by adding the same quantity of pesticide to the soil surface and leaching it under continuously ponded conditions, nematodes thrive at depths below 60 cm.

Although the solute distributions and their interpretations above support many of the six points made in this section, they remain empirical and speculative owing to the fact that such distributions cannot at this time be accurately predicted based upon our present knowledge of soil hydrology. Different results will no doubt be obtained for different soils, solutes and local conditions. Even for the above experiment, had the intermittent applications of water been made at intervals greater than one week, entirely different results would have occurred. That is, it is known based upon the analysis of the soil water behavior in this study (Nielsen et al., 1967) that at the end of one week, evaporation at the soil surface together with gravitational redistribution of soil water allowed a net vertically upward movement of water from the 90-cm soil depth. Hence, at those smaller soil water contents and water flux densities, the chloride would have started to move more efficiently to the soil surface. In such a case, continually ponding the soil surface would have more efficiently leached the soluble solute per unit water infiltrated from the 150-cm soil profile.

Fig. 9.29 shows an example of the chloride concentrations measured within the soil profiles from which the distributions given in Fig. 9.28 were derived. The figure pertains to the intermittently 15-cm ponded treatment for soil depths of 30, 90 and 150 cm. A distinctive characteristic of the curves for the 30- and 90-cm depths is the relative minimum reached soon after the initiation of each 15-cm water application. Similarly, a relative maximum is reached near 400 h soon after the third 15-cm water application. This behavior is associated with the sampling technique. When soil solution is extracted, the bulk of the flow takes place in the larger water-filled pore sequences. Hence, at the shallower depths, the more solute-free infiltrating water flowing through the larger water-filled pores and extracted by the soil solution samplers during infiltration yields a solution that is, indeed, more dilute than the average solute concentration at that depth. Similarly, the more concentrated solution from the shallower depths temporarily taken into the soil solution samplers at the greater depth is greater than the average solute concentration at that depth.



Figure 9.29. Chloride concentration distributions measured at depths of 30, 90 and 150 cm. Zero time represents the time when the first 15-cm ponded water application was initiated. The vertical arrows indicate the other times when additional 15-cm applications were initiated.

Acknowledging that the efficiency of solute leaching obeys the principles discussed here, Dahiya et al. (1985) nevertheless recommend that leaching of saline soils be carried out under continuously ponded conditions based upon their experiments with different plot sizes. They argue that under practical situations in which reclamation is carried out in large field domains, controlled slower, uniform infiltration at smaller soil water contents would require more labor and time.

Except for the post script that follows, we conclude our book with the admonishment that observations and theories of soil hydrology have not yet completely reconciled different scales of space and time in the management of fresh water retained at continental surfaces.

PROBLEMS

- Considering a soil column in the laboratory to be equivalent to a bundle of independent capillary tubes, calculate breakthrough curves similar to that shown in Fig. 9.5b for a. a column composed of equal-sized capillary tubes and b. a column composed of two tubes of radius 0.1 cm and 4000 tubes of radius 0.001 cm. Discuss your answer in terms of "preferential flow".
- 2. By changing variables (X, t) of (9.24) to [(z vt), t] and substituting D_a for D, derive (9.42).
- 3. Assume that (9.44) describes a pulse of solute ($t_1 = 0.4$ d) being leached through a homogeneous, water-saturated soil column of length 2 m. For an average pore water velocity v = 40 cm·d⁻¹, you measured at z = 1 m a

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relative maximum concentration $[(C - C_i)(C_o - C_i)^{-1}] = 0.22$. What is the value of D_a ? Hint: First obtain $\partial C / \partial z$ and set it equal to zero.

- 3. a. Experimentally for the above problem, how could you best establish the boundary condition $C = C_o [0, (0 < t \le t_1)]$? b. Similarly, how could you best experimentally establish the constant solute flux density boundary condition $[vC D_a \partial C / \partial z = \text{constant})$ at z = 0? In each case, explain the limitations of alternative techniques.
- 4. Show that for large values of $v D_a^{-1}$, (9.44) reduces to

$C-C_i$	1 arto	z-vt	orfo	$z-v(t-t_1)$	
$\overline{C_0 - C_i}^{-2}$	$2 \left[\frac{e^{ij}}{2} \right]$	$\left[\left(4D_a t \right)^{1/2} \right]$		$\left[4D_a(t-t_1)\right]^{1/2}$	ſ

Hint: $\lim \exp(x) \operatorname{erfc}(x) = 0$.

- 5. You are interested in simulating with (9.44) the spreading of a solute pulse (initially of thickness $vt_1 = 15$ cm in the topsoil) moving below plant roots in the vadose zone of a semi-arid environment. The long-term average net amount of water moving past the zero flux plane in the soil profile is only 0.01 cm d⁻¹. You first assumed that $D_c \gg D_m$ and approximated D_a in (9.44) by βv using a published field-estimated value of the dispersivity $\beta = 3$ cm. Next, you assumed that $D_c = D_m = 0.6$ cm²·d⁻¹. a. With your first assumption, calculate the distribution of the solute $\{[C(z) - C_i][C_o - C_i]^{-1}\}$ in the vadose zone for times t = 100 and 1000 y. b. With your second assumption, calculate the distribution of the solute $\{[C(z) - C_i][C_o - C_i]^{-1}\}$ in the vadose zone for the same times. Which assumption do you believe is more realistic, and why?
- 6. Discuss the implications of using temporal and spatial average values of D_a and v in the above problem.
- 7. The term ϕ_i in (9.35) sometimes represents the growth of soil microbes with the Michaelis-Menten process having the form

$$\phi_i = \frac{\kappa_m C}{K_m + C}$$

where κ_m is the product of a maximum growth rate constant and the biomass of the microbes and K_m is a "saturation" constant. a. For a concentrated soil solution, show that the above equation reduces to a zero-order equation with a constant value $\phi = k_o$. b. For a dilute soil solution, show that the above equation reduces to a first-order equation with $\phi = kC$ as was assumed in (9.52).