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Water Flow and Solute Transport Processes in the Unsaturated Zone

D. R. NIELSEN

Department of Land, Air, and Water Resources, University of California, Davis

M. TH. VAN GENUCHTEN

U.S. Salinity Laboratory, U.S. Department of Agriculture, Agricultural Research Service, Riverside, California

J. W. BIGGAR

Department of Land, Air, and Water Resources, University of California, Davis

This paper gives a review of our current conceptual understanding of the basic processes of water flow and chemical transport in the unsaturated (vadose) zone and of various deterministic mathematical models that are being used to describe these processes. During the past few decades, tremendous effort has been directed toward unravelling the complexities of various interactive physical, chemical, and microbiological mechanisms affecting unsaturated flow and transport, with contributions being made by soil scientists, geochemists, hydrologists, soil microbiologists, and others. Unfortunately, segmented, disciplinary research has contributed to a lack of experimental and theoretical understanding of the vadose zone, which, in turn, has precluded the accurate prediction and management of flow and contaminant transport through it. Thus a more unified and interdisciplinary approach is needed that considers the most pertinent physical, chemical, and biological processes operative in the unsaturated zone. Challenges for both fundamental and applied researchers to reveal the intricacies of the zone and to integrate these with currently known concepts are numerous, as is the urgency for progress inasmuch as our soil and ground water resources are increasingly subjected to the dangers of long-term pollution. Specific research areas in need of future investigation are outlined.

1. INTRODUCTION

The water unsaturated zone of the earth's crust remains an enigma to scientific understanding and technological management. Alternative names are the vadose zone and the partially saturated zone, being the land region bounded at its top by the soil surface and below by the ground water table. Ignoring entrapped or dissolved air, the unsaturated zone constitutes that part of the soil profile where water contents are less than the soil porosity, or in a more formal sense, where the soil water pressure (or matric) potential is negative, being less than that of free water at the same location and of the same temperature and ionic composition as the soil solution. The latter definition considers the water-saturated capillary fringe region immediately above the water table as an integral part of the unsaturated zone. We also consider temporary water saturation due to surface ponding or associated with perched water tables within the scope of unsaturated flow and transport. Finally, we assign the same meanings to the terms "vadose zone" and "unsaturated zone," while realizing that some have used the term vadose zone to refer more specifically to relatively deep and/or highly unsaturated geologic profiles, especially in arid and semiarid regions.

The unsaturated zone is inextricably involved in many aspects of hydrology: infiltration, evaporation, groundwater recharge, soil moisture storage, and soil erosion. It also contributes to the spatial and temporal distributions of plant communities under naturally occurring rainfed conditions and serves as a modifying influence on the production of cultivated crop species. Thus the vadose zone represents the conduit through which liquid and gaseous constituents are attenuated and transformed as they are exchanged in both directions between the soil surface and the water table.

During the past decade, the impetus to understand and manage the unsaturated zone stems from its recognition as a key factor in the improvement and protection of the quality of groundwater supplies. Surface and groundwaters are linked by the unsaturated zone. In the past, as well as in the present, surface waters were often diverted and managed without sufficient regard to the impact on ground water and vice versa. Liquid and solid waste disposal sites, once believed to permanently contain their contents, are now known to leak. The migration of fertilizers and pesticides from agricultural and domestic usage, of solvents and toxic substances from industrial usage, and of countless other inorganic and organic chemicals into the topsoil and through the unsaturated zone has signalled the pollution of groundwater. As a result, state and federal legislation has initiated measures to control or regulate the kinds of chemicals being released directly or indirectly into the soil surface and to identify and delineate local environmental conditions that mitigate against chemical transport. The measures seldom take into account the physical, chemical, and biological nature of the vadose zone within which chemicals and their metabolites are expected to interact.

The ambiguity of the unsaturated zone stems from the fact that it has not been the consistent focus of attention of any scientific discipline or any sector of society as regards its conservation, use, or management. Biological research for agriculture and silviculture considers its top boundary primarily as a cyclic source of water and plant-essential nutrients. The focal point of that research is the transformation of solar energy and the absorption of inorganic constituents to enhance the biotic potential of a region. Crop yield is foremost, with the alteration of the underlying vadose environment seldom con-

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sidered. Groundwater hydrologists hold two traditional views of the unsaturated zone. One is that it serves as a buffer for runoff and erosion through its potential to absorb water infiltrating from rainfall. The other view is that it serves as a source of water that reaches the water table at a rate equal to the difference between infiltration and evapotranspiration. Both viewpoints generally ignore those properties of the unsaturated zone that impinge on the quality of the water, which, in turn, has a direct influence on the retention and transmission of vadose water. Geochemists tend to concentrate on chemical equilibria pertaining to the unsaturated zone, or on the relative isotopic abundances of naturally occurring or human-released elements for age dating or estimating transfer processes within the earth. Owing to the dearth of readily available carbon sources usually encountered in the unsaturated horizons below the root zone of plants, microbiologists have not been inclined to extensively investigate the nature of its microbial communities.

Hence segmented, disciplinary research contributes to our lack of theoretical and experimental understanding of the vadose zone and precludes the prediction and possibly management of the rate of advance of gaseous or liquid constituents through it. The challenges for both fundamental and applied research to reveal the intricacies of the zone are numerous and await those having an education and curiosity of sufficient magnitude to respond. Our purpose here is to describe the general nature of the zone, to state those theoretical concepts believed to be applicable, and to outline possibilities for future investigation. A major message of this paper is our belief that present work on flow and transport lacks a unified approach that includes all pertinent physical, chemical, and biological processes operative in the unsaturated zone. While this message suggests that water flow and solute transport phenomena should be treated simultaneously, we nevertheless elect for organizational convenience to discuss first liquid flow and then to deal more specifically with solute transport processes. We also remind the reader that this presentation is based on the authors' experiences, with references cited to illustrate their viewpoints. The references, in spite of their large number, do not reflect a complete, comprehensive developmental or historical review of the subject. Finally, this paper focuses primarily on conceptual and mathematical, deterministic aspects of vadose zone flow and transport processes. We fully recognize that any realistic field-scale modeling exercise must also deal with the natural variability and heterogeneity of field soils. We refer to the paper by *Dagan* [this issue] for a detailed treatment of this problem.

2. Physicochemical Observations

The liquid in the vadose zone is not pure, but is a solution of water and dissolved solid and gaseous constituents. Moreover, soil water cannot be considered simply as ordinary water with a few dissolved solutes, since soil water properties are intimately linked to the chemical and physical properties of the solid phase on which it is sorbed [*Nielsen et al.*, 1972]. The impact and degree of this linkage hinge on the amount of water that is in the soil and on the mineralogical composition and particle-size distribution of the solid phase. The physical properties of vadose water may differ at times markedly from those of water that fills the relatively large pores of highly permeable groundwater aquifers because water is a strong dipole and is readily influenced by the net surface charge density of the soil particles and the numbers and kinds of dissolved constituents. Solution ions satisfy the surface charge on

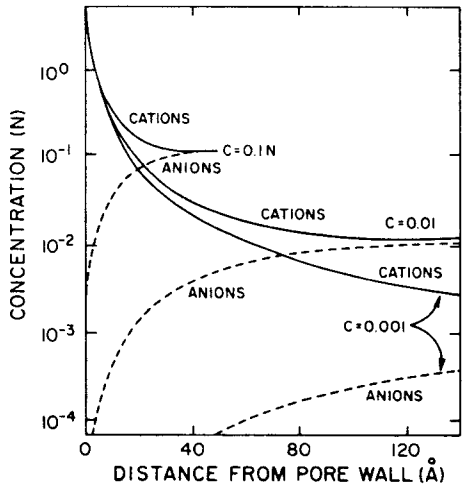

Fig. 1. Distribution of monovalent cations and anions near the surface of a montmorillonite particle [after *Nielsen et al.*, 1972].

soil particles caused by isomorphous substitution of one element for another in the crystal lattice of clay minerals, by ionization of hydronium of hydroxyl ions at the surface edges of clay particles, and other mechanisms. The net surface charge of an assemblage of soil particles gives rise to an electrical field that affects the distribution of cations and anions within the water films. It may also change the configuration and properties of the water close to particle surfaces, although some controversy still exists about the extent to which physical properties of water are effected by interactions with the solid phase, as well as the significance of these effects to macroscopic soil behavior [*Parker*, 1986]. Figure 1 shows distributions of monovalent ions in the soil solution as a function of distance from the soil particle surface within a water-saturated soil pore. For the more concentrated solution of 0.1 N the impact of the electrical field is not evident at distances greater than about 5 nm, while that for the dilute solution (0.001 N) extends further than 20 nm into the pore. The thickness of the electrical "double layer" that neutralizes the excess surface charge of soil particles is not only affected by the total electrolyte concentration, but also by the mineralogical composition of soil particles and by the valency and hydration of ions in the soil solution. For example, the extent of the double layer as shown in Figure 1 tends to be less for divalent than monovalent ions; details can be found in standard textbooks (*van Olphen* [1963]; *Bolt* [1979]; *Sposito* [1984]; among others).

The distributions in Figure 1 are for a water-saturated soil. As the water content decreases, the cations and anions are forced to occupy a space limited by the thickness of the water films on the soil particle surfaces. Such a surface-related phenomenon may give rise to swelling pressures [*Bolt and Bruggenwert*, 1976], streaming potentials [*Bolt*, 1979], and salt sieving [*Kemper*, 1960]. It is well known, even for water-saturated conditions, that the hydraulic conductivity of a soil can change an order of magnitude by merely altering the concentration or the kinds of cations associated with the charged soil particles (see section 3.3). Compared with water-saturated conditions when pores and water lenses have thicknesses on the order of 10^3–10^4 molecules of water, water–solute–particle surface interactions become increasingly more important as the soil becomes progressively drier. The interactions are sig-

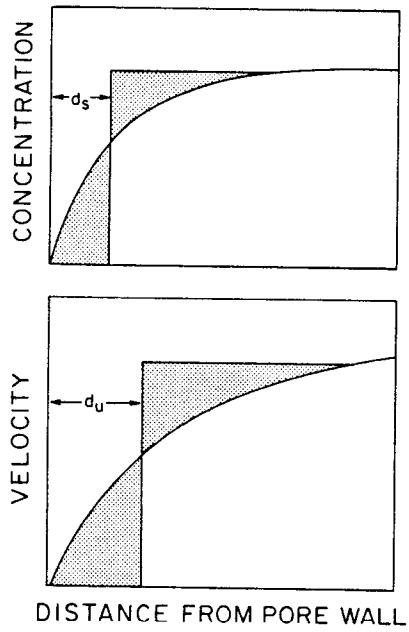

Fig. 2. Idealized version of the anionic concentration (top) and velocity distribution (bottom) within a soil pore. The distances d_s and d_u are defined by the vertical lines that divide the nonlinear portions of the distributions into two equal areas [after *Krupp et al.*, 1972].

nificant when water contents in the vadose zone reduce to equivalent water films of up to only 10–20 molecules thick. A detailed review of this topic is given by *Parker* [1986].

The solute distributions given in Figure 1 are applicable to the condition that the soil water is stagnant; i.e., the soil water flux is zero. If the soil water is not stagnant, the water velocity distribution within a soil pore manifests a relative maximum in the center of the pore and minimal values at the pore wall (Figure 2 (bottom)). For a homogeneous fluid in a cylindrical pore and assuming zero shear at the pore wall, the water velocity distribution can be considered parabolic according to the Hagen-Poisseuille equation. In the case of soil, the wall is charged and the physical properties of soil water are a function of the distance from the pore wall. Hence the actual velocity distribution in Figure 2 (bottom) is only approximately parabolic, and indeed may change with the average concentration or with different proportions of solute species in the soil water. There are few, if any, solutes within the thin water films of the vadose zone that do not interact in some way with soil-particle surfaces. Also, as the thickness of the water film changes, the relative rates of movements of the tracer and the water also change. This is illustrated in Figure 2, which shows hypothetical distributions of anions and water velocities adjacent to a negatively charged surface within a single soil pore. The distance d_s represents the idealized portion of the pore that contains no solute if the actual distribution is approximated with an equivalent step function, while d_u is the idealized portion of the water that is stagnant [*Krupp et al.*, 1972]. The relative rates of water and solute moving through the pore depend on the relative values of d_s and d_u. If, indeed, $d_u < d_s$, salt sieving occurs [*Bolt*, 1979]. The magnitudes of d_s and d_u depend on the concentration and kinds of ionic species in the soil solution, the thickness of the water films, and the soil-water flux. Similar considerations hold for cationic, polar, and nonpolar solutes.

Because of the complexities indicated above, a description of the forces acting on the vadose water to predict its retention and movement cannot be restricted, as it generally is for groundwater aquifers, to those stemming from the earth's gravitational field. Since the net force may be regarded as the gradient of a scalar potential, we define the soil water potential Ψ_t in energy per unit mass (joules/kg) for isothermal conditions as

$$\Psi_t = \sum_i \Psi_i = \Psi_p + \Psi_s + \Psi_e + \Psi_z \tag{1}$$

where Ψ_p is the pressure potential, Ψ_s the solute potential, Ψ_e the electrochemical potential, and Ψ_z the gravitational potential. This and other definitions of the soil water potential remain a piquant topic amongst investigators of unsaturated flow of soil water [*Sposito*, 1984; *Corey and Klute*, 1985]. Notice that the pressure potential Ψ_p is applied here to both the saturated and unsaturated zones. In the unsaturated zone, Ψ_p is generally negative and often termed the matric potential. The potentials above are expressed in terms of energy per unit mass. By multiplying with the density of water (ρ_w), potentials can also be expressed on a unit volume basis (joules/m^3), which is dimensionally the same as pressure (newtons/m^2 or pascals, Pa, in the SI system). Alternatively, potentials may also be expressed on a unit weight basis yielding dimensions of length (meter). Weight potentials are usually referred to as head and are derived from mass potentials upon division by the acceleration of gravity g. Thus the familiar pressure head h is given by $h = \Psi_p/g$.

Assuming that water moves proportionally to the forces acting on it, the rate at which water moves one dimensionally through the unsaturated zone is

$$q = -\sum_i K_i \frac{\partial \Psi_i}{\partial z} \tag{2}$$

where q is the volumetric flux density of water, z is distance, and K_i are proportionality coefficients that depend more or less on the degree of water saturation and temperature. For nonisothermal conditions, (2) becomes extremely complex [*Nielsen et al.*, 1972; *Raats*, 1975; *Milly*, 1982].

The obscurity of the vadose zone can be partially explained by the fact that both laboratory and field techniques for measuring Ψ_p, Ψ_s, and Ψ_e remain undeveloped or are limited to special conditions [*Black*, 1965]. Moreover, few direct means have been devised to measure q [*Dirksen*, 1972; *Cary*, 1973]; hence values of the transfer coefficients K_i have not been adequately evaluated or correlated with the composition of the vadose zone. In other words, methods for the direct measurement or calculation of the rate at which water moves through the vadose zone, based on its properties, have not yet been devised.

For most field studies to date, it is commonly assumed that Ψ_s and Ψ_e are spatially and temporally invariant. Combining (2) with the equation of continuity

$$\partial\theta/\partial t = -\partial q/\partial z + \Phi \tag{3}$$

leads to Richards' equation [*Richards*, 1931] for liquid flow in unsaturated soils. In terms of the pressure head, assuming a rigid medium, and taking the vertical spatial coordinate z positive downward the unsaturated flow equation becomes

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z}\right] - \frac{\partial K(h)}{\partial z} + \Phi \tag{4}$$

where θ is the volumetric water content; $C(h) \equiv \partial\theta/\partial h$ is the

water capacity or the slope of the soil water retention curve, $\theta(h)$; K is the hydraulic conductivity; t is time; while Φ represents sources and sinks of water in the system, notably those resulting from plant water extraction in the soil root zone. A close scrutiny of the theoretical basis of (4) reveals several assumptions that may be invalid for various field situations. For example, the equation ignores soil matrix and fluid compressibilities and assumes that the fluid density ρ_w is independent of concentration. Spatial variations in ρ_w are also taken to be insignificant. More importantly, (4) assumes that the air phase plays a negligible role in unsaturated flow processes and hence that a single equation can be used to describe unsaturated-saturated flow. A number of alternative two-phase flow models exist that explicitly consider simultaneous flow of water and air in soils; they are briefly reviewed in section 4.3. Equation (4) also assumes that Darcy's law (equation (2)), which was originally derived for saturated flow, can be extended to unsaturated conditions. Experimental evidence indicates that the equation may not be valid for fine-textured soils at low flow rates, with some suggesting that a threshold potential gradient exists below which no flow occurs [*Swartzendruber*, 1962; *Miller and Low*, 1963; *Bolt and Groenevelt*, 1969]. Darcy's law is also thought to be invalid at high flow rates when flow ceases to be laminar [*Childs*, 1969; *Bear*, 1972]. While flow in the vadose zone is usually of the laminar type, exceptions are likely during near-saturated flow in field soils exhibiting large continuous macropores (old root channels, cracked clay soils; aggregated soils). Unsaturated flow in structured field soils poses additional problems of geometry and flow continuity between interaggregate pores (or fractures) and intraaggregate pores (soil matrix). Depending on the scale at which flow calculations are made, the conventional flow equations may or may not be applicable to such structured systems. Currently, a number of alternative models are being explored in the literature. These models are briefly reviewed in section 4.4.

The term Φ in (4) relates to plant water absorption and is perhaps the most difficult one to quantify. While a large number of plant root extraction models exist, most or all are empirical or quasi-empirical using parameters that need to be adjusted for specific crop, soil, and environmental conditions. We elect not to further discuss root water extraction, and refer here only to a recent review by *Molz* [1981] for an inventory of various extraction terms that have been included in unsaturated flow models.

Assuming its applicability to field scale flow processes, (4) shows that the unsaturated hydraulic conductivity $K(h)$ and the soil water retention or characteristic curve $\theta(h)$ are the essential ingredients for predicting liquid flow in unsaturated soils. These two functions are closely examined next.

3. Unsaturated Soil Hydraulic Properties

With osmotic and electrochemical components ignored, and h measured with a tensiometer assuming solute equilibrium between the liquid solutions of soil and porous cup, a primary concern of soil hydrodynamicists has been the hysteretic behavior of the soil hydraulic functions $\theta(h)$ and $K(h)$. While hysteresis is an important phenomenon affecting liquid flow in soils and work in this area must continue, more emphasis needs to be given to the effects of temperature and soil salinity on the hydraulic properties. These and other effects are briefly discussed below.

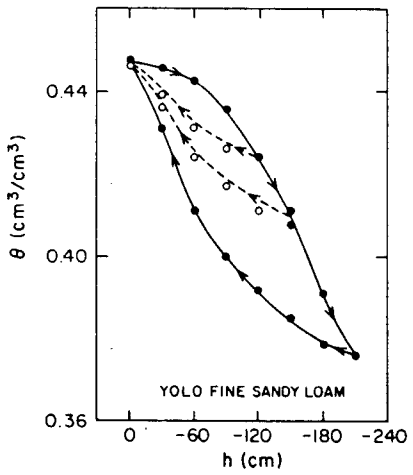

Fig. 3. Water retention curves for a sample of Yolo fine sandy loam. The solid curves are eye-fitted through measured data along the two main boundary curves. Dashed curves represent primary wetting scanning curves. Arrows indicate the direction at which the pressure head changes are imposed.

3.1. *Hysteresis Effects*

The hysteretic behavior of the soil water retention curve $\theta(h)$ is illustrated in Figure 3: the soil water content is not a unique function of h, but depends on the previous history of the soil. Hence any attempt to use (4) requires a description of $\theta(h)$ with sufficient detail to provide accurate estimates of the soil water capacity $C(h)$. The hysteretic nature of $\theta(h)$ is due to the presence of different contact angles during wetting and drying, and to geometric restrictions ("ink-bottle" effects) of single pores. The effects are usually augmented by the presence of entrapped air, by soil shrinking-swelling phenomena, and perhaps by rates of wetting and drying as well [*Davidson et al.*, 1966]. Similar hysteresis effects as in $\theta(h)$ are also present in measured $K(h)$ functions. Hysteresis in $K(\theta)$ is generally found to be less pronounced, but not necessarily negligible for all soils.

Hysteresis has important effects on water and solute distributions during field conditions that involve alternative wetting and drying. For example, after infiltration of a finite pulse of water, hysteresis tends to keep water contents higher in the initially wetted part of the soil, while simultaneously reducing the rate of advance of the wetting front in the drier soil below provided entrapped air effects [*Dracos*, 1984] at the deeper depths are insignificant. The concepts have been adequately explained in many textbooks [*Childs*, 1969; *Nielsen et al.*, 1972; *Bear*, 1972]. Various attempts have been made to describe hysteresis mathematically. Theoretical work initially concentrated on the independent domain theory in which only the geometry of pores determine the drying and wetting characteristics of each pore [*Everett*, 1954; *Enderby*, 1955]. Significant improvements were obtained by formulating dependent domain theories that allow for various interactions with neighboring pores [*Topp*, 1971; *Poulovassilis and Childs*, 1971; *Mualem*, 1974, 1984]. Notwithstanding the abundance of theoretical and empirical [e.g., *Scott et al.*, 1983] models, as well as the experimental evidence of hysteresis, the phenomenon has only sparingly been included in field scale flow and transport models. For typical examples, see *Giesel et al.* [1973] and *Pickens and Gillham* [1980].

3.2. *Temperature Effects*

Compared to hysteresis, the effects of temperature T on the hydraulic properties have been largely ignored. As early as 1915, *Bouyoucous* [1915] demonstrated that temperature affected pressure gradients in soil columns under isothermal conditions. *Moore* [1940] subsequently showed that T has a considerable effect on the soil hydraulic properties, in part through its direct effect on viscosity and surface tension. However, he also noted that factors other than viscosity affected soil water retention and liquid flow. Since then, only a handful of researchers have studied the temperature effect in detail. This is surprising considering the fact that for some soil and environmental conditions temperature can exert a greater influence on water content than the pressure potential [*Taylor and Stewart*, 1960]. Known effects of T on $\theta(h)$ and $K(\theta)$ are illustrated in Figures 4 and 5, respectively. Figure 4 shows for three soils that at a given pressure potential, less water will be retained when T increases. The influence is especially significant for fine-textured soils. Temperature effects can be explained in part by changes in surface tension which causes an increase in the pressure head with increasing temperature [*Philip and de Vries*, 1957]. However, experimental evidence indicates that observed temperature effects on $\theta(h)$ can be up to 10 times greater [*Hopmans and Dane*, 1986]. Explanations for the larger than expected changes in the hydraulic properties include effects caused by entrapped air, the presence of contaminants affecting surface tension at the air-water interface, temperature-induced structural changes, and perhaps by changes in the diffuse double layer, although recent experiments by *Smiles et al.* [1985] suggest that the anomaly may not result from indirect double layer effects.

Several researchers have sought to explain the temperature dependency of the hydraulic conductivity (Figure 5) through the temperature dependency of the viscosity. To do so, $K(\theta)$ is partitioned into the form [*Constantz*, 1982]

$$K(\theta) = k_r(\theta) k \rho_w g / \mu_w \tag{5}$$

where $k_r(\theta)$ is the relative conductivity ($0 \le k_r \le 1$); k is the intrinsic permeability; and μ_w is the dynamic viscosity of soil water. Because temperature has a negligible effect on ρ_w, its influence on K can be explained only through changes in the viscosity μ_w. Conflicting evidence [*Flocker et al.*, 1968; *Rahi and Jensen*, 1975; *Constantz*, 1982; *Hopmans and Dane*, 1986] exists as to whether this dependency is sufficient to explain the totality of the temperature effect on K, with some suggesting that there should also be an effect through $k_r(\theta)$. This disagreement should motivate additional work in this important but neglected area of research. We note here that the temperature effects shown in Figures 4 and 5 are for otherwise isothermal conditions and hence should be included in flow models in addition to the more direct effects caused by nonisothermal liquid and vapor flow.

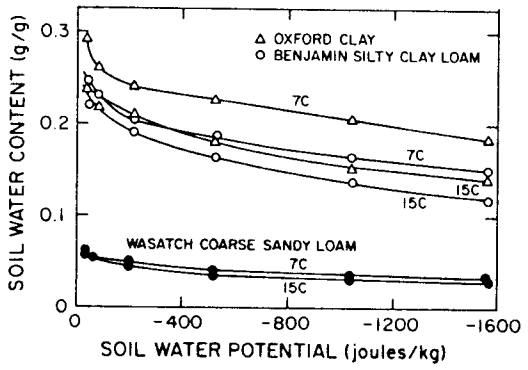

Fig. 4. Soil water retention curves for three soils at two temperatures [after *Taylor*, 1958].

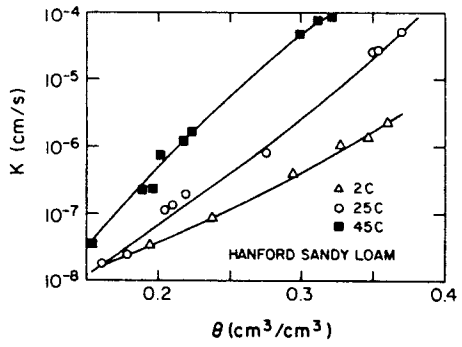

Fig. 5. Unsaturated hydraulic conductivity K as a function of water content θ at three temperatures [after *Constantz*, 1982].

3.3. *Salinity Effects*

The hydraulic properties, especially those of fine-textured soils, are also greatly affected by the total concentration and ionic composition of the soil solution. Of the cations commonly found in natural waters, Na^+ is most likely to adversely affect the hydraulic properties. This cation increases the extension of the electrical double layer (Figure 1), which, in turn, causes swelling between individual platelets of clay particles. Sodium also tends to weaken bonds between clay particles by increasing the repulsive forces between them. This leads to the detachment of small clay particles from larger units and their transport and subsequent settlement in pore restrictions (clogging). All this causes a shift in the pore-size distribution by decreasing the number and size of the larger interaggregate pores and increasing the number of smaller pores in the system. The net result is usually a reduction in the hydraulic conductivity at any given water content and an increase in water content at a given pressure head, except perhaps near saturation if soil swelling is limited by a constant porosity in the field. Reductions in $K(\theta)$ are often only partially reversible [*McNeal and Coleman*, 1966; *Dane and Klute*, 1977]. While both soil swelling and particle displacement contribute to changes in K, the relative importance of the two processes is still being debated. For a recent review of experimental evidence, see *Shainberg* [1984].

Factors that contribute most to reductions in the hydraulic conductivity parallel those that increase the extent of the electrical double layer: low electrolyte concentrations, high values of the exchangeable sodium percentage (ESP) or the sodium adsorption ratio (SAR), and increased amounts of expansive 2:1 phyllosilicate minerals (montmorillonite and illite). The effect of total salinity on the unsaturated hydraulic conductivity $K(\theta)$ is illustrated in Figure 6. Figure 7 shows transient changes in the saturated hydraulic conductivity K_s during leaching with distilled water. The experiments were repeated for three different soils that were initially equilibrated with 0.05 M solutions at different SAR. *Shainberg et al.* [1981] hypothesized that differences in K_s reductions amongst the soils in Figure 7 were caused by different mineral dissolution rates due to weathering. High weathering rates contribute to the maintenance of critical solute levels and thus to a lesser

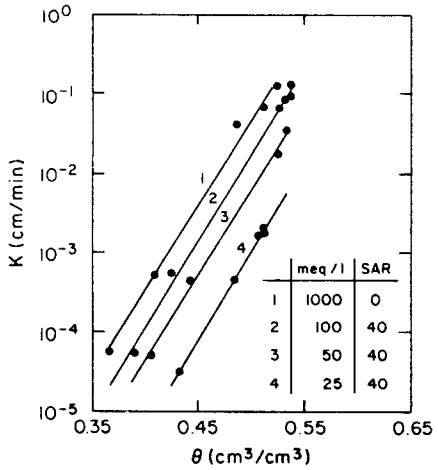

Fig. 6. Hydraulic conductivity K as a function of water content θ of a Weld soil sample subjected to several solutions of decreasing concentration and at SAR = 40 [after *Dane and Klute*, 1977].

reduction in K_s in response to exchangeable sodium. *Suarez et al.* [1984] also demonstrated an important effect of *p*H on the hydraulic conductivity. This last effect is illustrated in Figure 8, which shows for several *p*H values the relationship between SAR and total electrolyte concentration at which the K_s decreased by 50%. Reductions greater than 50% occurred at higher SAR values and/or lower total concentrations (above and to the left of the curves). Increasing *p*H has an adverse effect on K, presumably due to charge reversals from positive to negative of oxide minerals in the soil, and edge charge reversal of clay minerals with subsequent breakage of edge to face bondings.

Hydraulic conductivity reductions can become dramatic during rainfall on fine-textured soils with relatively high SAR values. Rainwater is nearly always below 0.3 meq/L [*Hem*, 1970], in contrast to most surface waters which are typically above 3 meq/L. Structural changes at the soil surface that lead to soil crusting are hence more prevalent during rainfall conditions as compared to irrigation with surface waters. Such physical processes as soil tillage, raindrop impact, traffic, and wetting-drying or freezing-thawing cycles at the soil surface further contribute to soil structural changes, and hence to changes in the $K(\theta)$. Because of the significant effects of concentration and ionic composition on the hydraulic conductivity, attempts must be made to include them in existing flow and transport models. While we acknowledge the difficulty of quantifying the many coupled and time-dependent processes

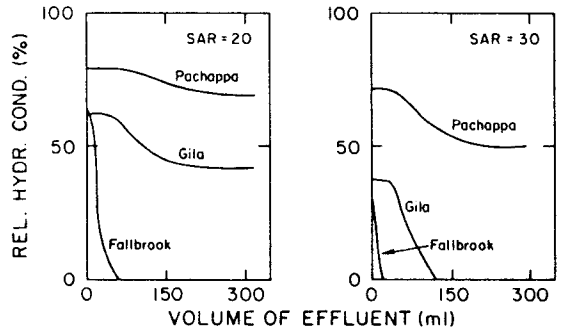

Fig. 7. Changes in the saturated hydraulic conductivity of three soils that were first equilibrated at different SAR's and then leached with distilled water [after *Shainberg et al.*, 1981].

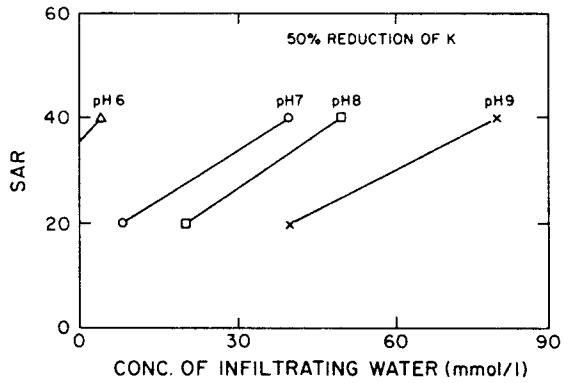

Fig. 8. Effect of *p*H on the relationship between SAR and solute concentration for Bonsall soil when the hydraulic conductivity K_s was reduced by 50% [after *Suarez*, 1985].

into a unified theoretical approach, the challenge is there. Several empirical and more analytical attempts have been made to quantify the above interactions on K_s at the microscopic level [*McNeal and Coleman*, 1966; *Lagerwerff et al.*, 1969]. These attempts differ radically from more macroscopic formulations that consider liquid flow in swelling soils without regard to specific ionic interactions between the soil solution and the porous medium [*Philip*, 1969; *Smiles*, 1974; *Miller*, 1975; *Sposito and Giraldez*, 1976]. A conceptually appealing alternative, based on double layer theory and pore-size distributions, was suggested by *Russo and Bresler* [1977]. Again, potential payoffs of systematic research in this area, especially one that integrates the relevant physical and chemical processes, could be significant.

3.4. *Determination of the Hydraulic Properties*

While the soil water retention and hydraulic conductivity functions are the crucial parameters for predicting unsaturated flow, their theoretical description and measurement remains a continuous and sometimes frustrating challenge for hydrologists and soil scientists. Numerous methods have been developed to evaluate the hydraulic properties using both in situ field and laboratory procedures. The need for accurate, yet economical methods is not likely to diminish in view of recent awareness that the functions are subject to important temporal and spatial variations in the field. While in situ field measurements undoubtedly are the most representative of actual flow conditions, current methods are likely to remain approximate in nature. This is due in part to simplifying assumptions inherent in most field methods, and in part to problems of obtaining undisturbed samples. Field methods usually require the use of tensiometers for the measurement of hydraulic gradients and the estimation or measurement of water contents using gravimetric, neutron, or gamma ray techniques [*Black*, 1965; *Morrison*, 1983]. Most current methods are based on simplifying assumptions about the flow regime during redistribution of soil water after reaching saturated or near-saturated steady state flow. Nevertheless, a number of field methods are now available that allow for a quick and reasonably easy in situ measurement of the hydraulic conductivity (*Fluehler et al.* [1976]; *Libardi et al.* [1980]; *Sisson et al.* [1980]; *Chong et al.* [1981]; among others). Reviews of both laboratory and field experimental methods are given by *Klute* [1972] and *Bouwer and Jackson* [1974].

Recently, interest has arisen in the feasibility of determining water retention and hydraulic conductivity functions simulta-

neously from transient flow data by parameter estimation [*Zachmann et al.*, 1981; *Dane and Hruska*, 1983; *Hornung*, 1983; *Kool et al.*, 1985]. The parameter estimation procedure assumes that hydraulic properties can be described by known mathematical functions with a small number of parameters. With some flux-controlled attribute being measured at a number of times or depths and the flow problem is simulated numerically using initial and updated parameter estimates until an optimum match between observed and simulated response is obtained. The methodology appears promising, although problems of computational efficiency, convergence, and parameter uniqueness [*Kool et al.*, 1986] remain unresolved.

3.5. *Mathematical Models for the Hydraulic Properties*

Direct field methods to determine the unsaturated hydraulic conductivity are time consuming, expensive, and usually subject to simplifying assumptions. An attractive alternative to direct measurement is the theoretical calculation of the hydraulic conductivity from more easily measured field or laboratory soil water retention data. A theoretical basis for this approach was derived by *Childs and Collis-George* [1950]. Their relation was based on a cut and random rejoin pore model that accounts for the probability of distinct pore size classes to overlap each other. Various modifications and refinements of this model were presented by *Burdine* [1953], *Marshall* [1958], and *Millington and Quirk* [1961]. An analogous model that also considers changes in the pore size distribution with distance was later introduced by *Mualem* [1976]. A somewhat different approach based on the particle size distribution of a granular medium was described by *Arya and Paris* [1981].

The above predictive theories for $K(\theta)$ require accurate descriptions of the soil water retention curve. Particularly useful are analytical (nontabular) functions that enable their efficient inclusion in simulation models and also allow for a rapid comparison [*Rawls et al.*, 1983] or scaling [*Simmons et al.*, 1979*a*, *b*] of the hydraulic properties of different soils. While a variety of empirical functions exist [*Brooks and Corey*, 1964; *Rogowski*, 1971; *Farrell and Larson*, 1972], only a few possess the phenomenological properties that are typical of observed field data. For example, several models are based on the premise of a well-defined air-entry value h_a that induces a sharp break in the $\theta(h)$ and $K(h)$ curves close to saturation. While such a parameter is physically realistic for certain coarse-textured soils with relatively narrow pore-size distributions, its existence for most field soils having much broader pore-size distributions must be questioned [*van Genuchten and Nielsen*, 1985]. Among the retention equations that have realistic shapes and curvatures are equations proposed by *King* [1965], *Visser* [1968], *Laliberte* [1969], *Gillham et al.* [1976], *Varallyay and Morinenko* [1979], and *van Genuchten* [1980]. For example, van Genuchten's equation is given by

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} \tag{6}$$

where θ_r and θ_s are residual and field-saturated volumetric water contents, respectively, h is the pressure head, and α, n, and m are empirical constants. In practice, also θ_r and θ_s must be considered empirical [*van Genuchten and Nielsen*, 1985]. Using the simplifying assumption that $m = 1 - 1/n$, (6) can be combined with the predictive conductivity model of *Mualem* [1976] to yield an expression for $K(S_e)$ of the form

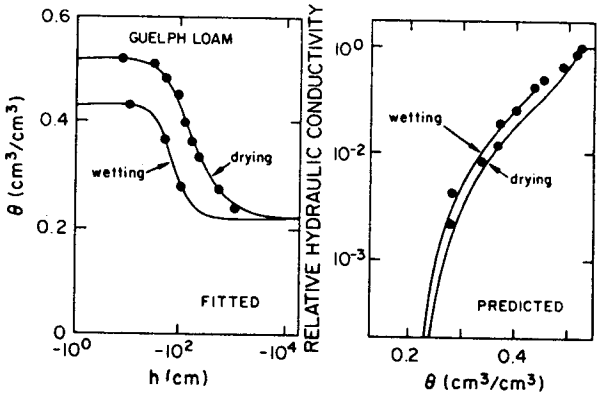

Fig. 9. Observed (circles) and calculated curves (solid curves) of the soil hydraulic properties of Guelph loam. The drying and wetting branches of the relative hydraulic conductivity curve were predicted from the curve-fitted branches of the soil water retention curve.

$$K = K_s S_e^{\,l}[1 - (1 - S_e^{\,1/m})^m]^2 \tag{7}$$

where $S_e = (\theta - \theta_r)/(\theta_s - \theta_r)$ is the effective saturation, and l is an empirical parameter that was estimated by Mualem to be approximately 0.5 for most soils. Figure 9 gives an example of the type of predictions that were obtained with this equation. Like previous predictive models, (7) works well for medium and coarse-textured soils, with predictions for fine-textured materials generally being less accurate.

While much work has already been invested in their development, we believe that the potential of predictive hydraulic conductivity models has not yet been fully explored. Because of the spatial and temporal variability problem, it is not unlikely that predictive models eventually, or perhaps already, yield estimates for the hydraulic functions that are sufficiently accurate for many field applications.

4. Unsaturated Flow Predictions

Numerous analytical and numerical solutions of the unsaturated flow equation (equation (4)) have been developed over the last 30 years or so to the point that at present certainly no scarcity exists in one- and multidimensional models. Early modeling attempts were mostly based on finite difference schemes, followed in the late 1960s by various finite element methods, and more recently by integrated finite difference approximations. Several useful analytical solutions have also been derived. Only a brief review of the modeling work is given here. More extensive reviews and model inventories of unsaturated and partly saturated flow models are given by *Narasimhan and Witherspoon* [1976], *Oster* [1982], and *van der Heijde et al.* [1985]. We will conveniently distinguish between analytical and numerical solutions and also briefly discuss two-phase flow modeling of water and air and the modeling of flow in unsaturated structured systems.

4.1. *Analytical Solutions*

In the analytical approach, the governing equation, the unsaturated soil hydraulic functions, and the initial and boundary conditions are suitably simplified or approximated such that exact or "quasi-analytical" solutions can be derived. Initially, most solutions were applied only to one-dimensional, horizontal, or vertical systems. Highly significant is the early work of *Philip* [1955, 1957] that provided much of the physical and mathematical groundwork for subsequent analyses by

others. Numerous studies have followed for both one- and multidimensional problems (*Parlange* [1971]; *Babu* [1976]; *Warrick*, [1974]; *Raats* [1976]; *Lomen and Warrick* [1974]; *Batu* [1979]; among many others). While some of the solutions appear to be of only academic interest, others have or may prove to be useful for predicting unsaturated flow per se, or for several indirect applications, e.g., (1) for verification of numerical solutions, (2) for formulation of approximate inverse problems that lead to methods for measuring the unsaturated hydraulic properties, or (3) for deriving physically based expressions for infiltration rates in unsaturated soils [*Philip*, 1969; *Smith and Parlange*, 1978; *Knight*, 1983]. Lately, a promising alternative approach based on the method of characteristics has also been applied to gravity-dominated flow in the unsaturated zone [*Sisson et al.*, 1980; *Smith*, 1983; *Charbeneau*, 1984]; this approach is also useful in estimating the unsaturated hydraulic conductivity.

4.2. *Numerical Solutions*

While analytical solutions are useful for a number of applications, they are only applicable to highly simplified systems, and as such are not well suited for the more complex situations normally encountered in the field. Consequently, numerical solutions are often used. Initially, mostly finite difference methods were developed to predict unsaturated flow only. For typical examples, see *Hanks and Bowers* [1962], *Rubin and Steinhardt* [1963], and *Brandt et al.* [1971]. One and multidimensional finite difference schemes were subsequently developed that consider the dynamics of both the unsaturated and saturated zone in one scheme [*Hornberger et al.*, 1969; *Freeze*, 1969; *Cooley*, 1971; *Pikul et al.*, 1974]. The work by *Freeze* [1969, 1971*a*, *b*] in this period was especially significant since for the first time a single equation was used to describe transient unsaturated-saturated flow. The flow equation accounts not only for changes in water storage in the unsaturated zone, but also considers transient changes in the saturated zone.

Finite element solution techniques became available in the late sixties. They were initially applied only to saturated flow problems [*Javandel and Witherspoon*, 1968; *Zienkiewicz and Parekh*, 1970], but slowly became also popular for unsaturated flow problems (*Bruch and Zyvoloski* [1973]; *Neuman*, [1973]; *Reeves and Duguid* [1975]; *Frind et al.* [1977]; *Yeh and Strand* [1982]; *Huyakorn et al.* [1984]; among many others). A somewhat different integral solution procedure using "integrated finite differences" was introduced by Narasimhan and colleagues [*Narasimhan*, 1975; *Narasimhan et al.*, 1978].

Perhaps the most important advantage of finite element techniques over standard finite difference methods is the ability to more accurately describe irregular system boundaries in multidimensional simulations, as well as to more easily include nonhomogeneous medium properties. Several authors have also suggested that finite element methods lead to more stable and accurate solutions, thus permitting larger time steps and or coarser grid systems, and hence leading to computationally more efficient numerical schemes [*Neuman*, 1973; *Reeves and Duguid*, 1975]. While this consideration may be true when the relatively linear solute transport equation is solved, conflicting evidence exists about the relative accuracy of finite element versus finite difference techniques with respect to solution of the highly nonlinear flow equation [*Pinder and Gray*, 1977; *Finlayson*, 1977; *Hayhoe*, 1978; *van Genuchten*, 1981*a*]. It appears that at least for one-dimensional simulations, finite difference methods are not better or worse than finite element schemes. With the introduction of increasingly sophisticated numerical models, the real challenge remains that of an accurate characterization of relevant system parameters, especially the unsaturated hydraulic functions.

4.3. *Two-Phase Water-Air Flow Formulations*

Equation (4) assumes that the effects of air pressure differences on unsaturated flow are negligible, thus permitting the use of a single equation to predict flow in the vadose zone. The assumption appears realistic for many unsaturated flow applications when soil air pressures deviate little from atmospheric pressure. Nevertheless, situations can occur where air is not free to escape when it is displaced by water, thus leading to larger soil air pressures and increased resistances to liquid flow. The most obvious situation is that of ponded infiltration over large areas, especially in the presence of high (or perched) water tables or relatively impermeable soil layers. Ponded infiltration may also lead to entrapment of air in soil aggregates, and thus invalidate the one-phase flow assumption. Hydrologists and soil scientists have studied the effects of air pressure by comparing infiltration rates and soil water distributions in soil columns that are open or closed to air [*Peck*, 1965; *McWorther*, 1971; *Vachaud et al.*, 1973]. Hydrologists also have long recognized the ramifications of air entrapment in shallow unconfined aquifers on unexpectedly large water table rises in observation wells [e.g., *Bianchi and Haskell*, 1966].

Initial theoretical descriptions of two-phase flow generally stem from the petroleum engineering literature [*Muskat*, 1949; *Douglas et al.*, 1959]. The following coupled system of equations, or simplifications thereof, has been applied to the two-phase water-air flow problem [*Green et al.*, 1970; *Morel-Seytoux*, 1973]:

$$\varepsilon \frac{\partial(\rho_w S_w)}{\partial t} = \frac{\partial}{\partial z}\left[k_{rw}\frac{\rho_w k}{\mu_w}\left(\frac{\partial \psi_w}{\partial z} - \rho_w g\right)\right] \tag{8}$$

$$\varepsilon \frac{\partial(\rho_a S_a)}{\partial t} = \frac{\partial}{\partial z}\left[k_{ra}\frac{\rho_a k}{\mu_a}\left(\frac{\partial \psi_a}{\partial z} - \rho_a g\right)\right] \tag{9}$$

where the subscripts w and a refer to the water and air phases, respectively, S is effective saturation, ψ represents pressures (potentials per unit volume), and ε is the soil porosity. Other symbols are as defined before. In particular note that the water (S_w) and air (S_a) saturations add up to unity. We refer to publications by *Morel-Seytoux* [1973], *Stroosnijder* [1976], and *Dullien* [1979] for additional discussions of (8) and (9), as well as for comprehensive reviews of various numerical and approximate analytical solutions. The approximations are perhaps most useful for formulating improved infiltration equations that include the effects of air entrapment.

As an illustrative example showing the effects of air entrapment, Figure 10 compares calculated and observed infiltration rates for 185-cm-long soil columns with and without provisions for air to escape at the bottom of the columns. Calculated curves were obtained with a slightly modified version of an approximate solution by *Brustkern and Morel-Seytoux* [1970]. Equations (8) and (9) have been applied here to the two-phase air-water flow problem. Similar two- or three-phase formulations are also applicable to the immiscible displacement of water, oil and gases, with important applications to organic chemical transport (section 6.4).

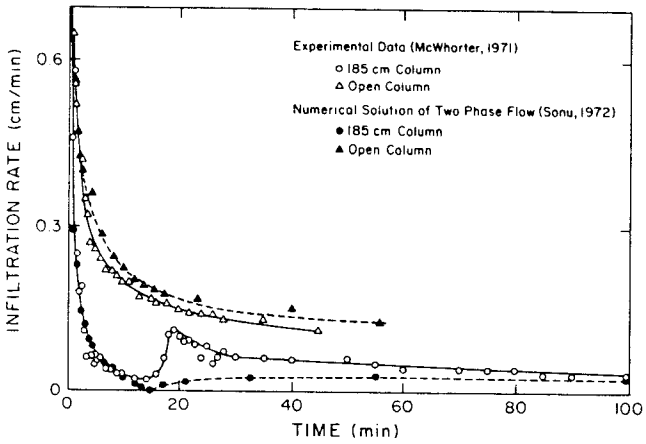

Fig. 10. Comparison of observed and calculated infiltration rate curves [after *Morel-Seytoux*, 1973].

4.4. *Flow in Unsaturated Structured Soils*

Recently, questions have arisen about the usefulness of (4) to describe unsaturated flow in structured soils. We use the term "structured soil" here to refer to soils that contain relatively large and more or less continuous voids, such as interaggregate pores, interpedal voids, earthworm and gopher holes, drying cracks in clay soils, decayed root channels, and other type of "macropores." Infiltration into and flow through such soils can be substantially different from that in relatively homogeneous materials. The effects of macropores in altering otherwise one-dimensional vertical unsaturated flow and transport has been convincingly documented in several recent review articles [*Thomas and Phillips*, 1979; *Bouma*, 1981; *Beven and Germann*, 1982; *Wierenga*, 1982; *White*, 1985]. Alternative terms used for macropore flow are channeling, short-circuiting [*Bouma and Dekker*, 1978], noncapillary flow, preferential flow, and bypassing, while the term fracture flow has been used mostly by groundwater hydrologists to indicate similar phenomena in saturated systems.

Attempts to describe flow in structured soils have generally centered on two-domain, two-region, or bicontinuum approaches. One domain consists of the soil matrix in which flow is described by the conventional, Darcian-based unsaturated flow equation, while the other domain consists of either a single macropore or of a statistical network of macropores through which water flows primarily under the influence of gravity. The two domains are connected through some common boundary condition, or by means of a simple source-sink term. Numerical solutions for these two-domain models, or simplifications thereof, are described by *Edwards et al.* [1979], *Hoogmoed and Bouma* [1980], *Yeh and Luxmoore* [1982], and *Davidson* [1985], among others. A somewhat analogous analytical formulation using kinematic wave theory to model liquid flow in the macropores was recently developed by *Germann and Beven* [1985]. *Wang and Narasimhan* [1985] presented a more sophisticated numerical solution for the drainage case that considers flow along partially desaturated rectangular macropores as well as flow between partially unsaturated soil matrix blocks.

As an illustrative example of the type of results that have been obtained thus far, Figure 11 shows calculated pressure head distributions in a soil with and without a hollow cylindrical macropore. Although the practical utility of many of the above cited two-region models remains unclear, the commitment of several researchers to the development of such models correctly reflects the importance that must be attached to macropore flows. While macropore flow has important effects on subsurface hydrology in general, and on infiltration rates and unsaturated soil water distributions in particular, its main implications are likely in the accelerated movement of surface-applied fertilizers or pollutants through the vadose zone. This last problem is discussed in more detail in section 6.3.

5. MECHANISMS OF SOLUTE TRANSPORT IN THE VADOSE ZONE

During the past 30 years, the major focus given to "hydrodynamic dispersion" or miscible displacement in porous media has been the examination of potential relationships between the dispersion tensor and the pore water velocity with the tacit assumption that the porous medium is inert and the solute or tracer is "nonreactive." And, after 30 years, with the hydrodynamicists continuing their propensity to focus on geometrical considerations of dispersion with the above assumption and geochemists focusing on chemical reactions ignoring the geometric effects, a major deficiency in our understanding of solute transport in the vadose zone persists. As with the hydraulic conductivity discussed previously, the deficiency reflects our inability to integrate simultaneously the most relevant physical, chemical, and biological processes in one theoretical framework.

We will first illustrate this interplay of several physical and chemical effects on transport with a data set from *Nkedi-Kizza* [1979], who used miscible displacement techniques to examine the movement of pulses of solution containing three tracers (^{35}Cl, $^{3}H_2O$, and ^{45}Ca) applied simultaneously to water- and calcium-saturated soil columns under a combination of four different parametric conditions. One parameter was that of the solution concentration being 0.1, 0.01, or 0.001 N. A second parameter was the *p*H of the soil system being 4, 7, or 9. The third parameter was that the soil was composed of water-stable aggregates having diameters of 0.5–1.0, 1–2, or 2–4.7 mm. The fourth parameter was that of the pore water velocity $v = q/\theta$. We utilize here only some of their data illustrated in

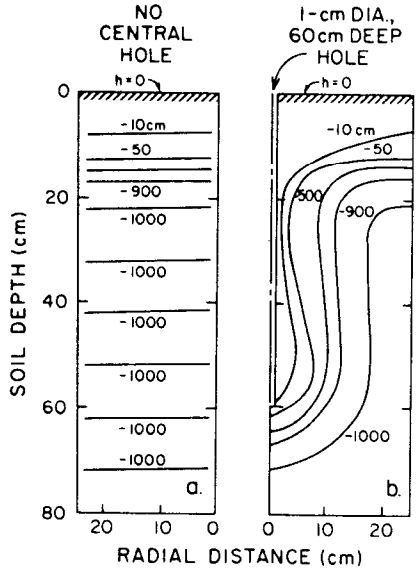

Fig. 11. Calculated pressure head distribution in 50-cm-diameter columns with no central hole (*a*) and with a central hole (*b*) at time = 0.5 hours [after *Edwards et al.*, 1979].

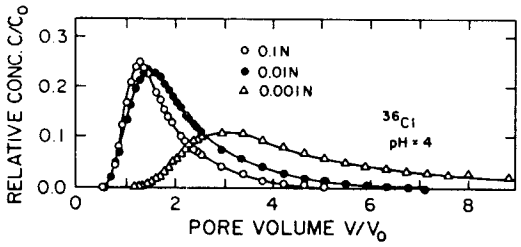

Fig. 12. Observed ^{36}Cl effluent curves showing the effect of total ionic concentration on the displacement process.

the next four figures. In Figure 12, as the concentration of the soil solution decreases, the breakthrough curves of ^{36}Cl shift to the right with their maxima decreasing. The data reveal that at *p*H 4, chloride is adsorbed. Owing to the fact that an equal number of negative and positive exchange sites exists at *p*H 3.6, we would expect both $^{36}Cl^-$ and $^{45}Ca^{2+}$ to be exchanged for their nonradioactive isotopes on the clay surfaces. Differences in shapes and positions of the curves in Figure 12 are therefore a result of the concentration of the soil solution rather than caused by hydrodynamic and geometric aspects of the flow regime.

As the *p*H of the variably charged soil monotonically increases above 3.6, the relative proportion of negative to positive exchange sites increases. Thus as is shown in Figure 13 for a constant soil solution concentration of 0.001 N, the ^{36}Cl breakthrough curve shifts to the left as the *p*H increases. At *p*H 9, the early breakthrough of ^{36}Cl is, indeed, indicative of a tracer that is repelled from the predominantly negatively charged clay surfaces. When quantifying adsorption-exchange processes, and in view of the experiments shown in Figure 13, it should be remembered that the surface charge characteristics of soil 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 charge of the former is permanent and independent of solution concentration. The charge of the latter is determined by the nature of the adsorbed ions, the concentration of the ions in solution, and the *p*H of the soil [*Keng and Uehara*, 1974]. 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 ion-exchange behavior under conditions that induce major shifts in *p*H cannot be ignored.

Figures 12 and 13 pertain to soil columns composed of 0.5- to 1.0-mm aggregates through which water was flowing at a constant flux of 0.9 cm/h. Figures 14 and 15 manifest the impact of water velocity and pore geometry, respectively. The higher flow velocity leads to an earlier breakthrough of the solute in the effluent. Larger aggregates similarly result in earlier breakthrough. Hence both flow velocity and aggregate size affect the transport rate, thus perhaps suggesting that the interactions between the soil and its solution are not at equilibrium under these conditions.

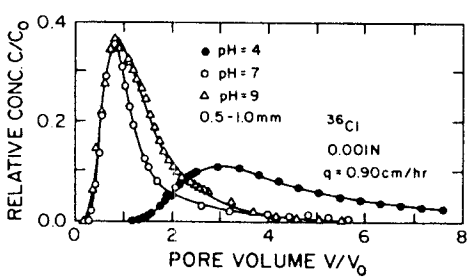

Fig. 13. Observed ^{36}Cl effluent curves showing the effect of solution *p*H on the displacement process.

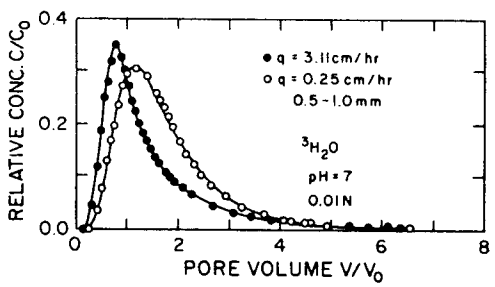

Fig. 14. Observed ^{36}Cl effluent curves showing the effect of water flux on the displacement process.

The data in Figures 12–15 were for a water-saturated soil. Similar data for unsaturated soils are not readily available. Even for saturated systems, the displacement of a solute through a soil having different proportions of cationic species (Na^+, Ca^{2+}, Mg^{2+}, etc.) on its exchange sites has not been extensively observed. Although such detailed experimental information is lacking for most soils, there is sufficient evidence in hand to suggest that the separately held conceptual views of the hydrodynamicist and the geochemist should be amalgamated into a more unified theory. It is, indeed, naive to consider that either water or its solutes can be within a field soil without being affected by soil particle surface interactions, or that the behavior of soil solutes can be described without considering the pore water velocity distribution. Thus for the discussions to follow it is imperative to understand that solute transport is impacted by both chemical and physical (including geometry-related) processes. Moreover, since many of these processes are only summarily known, if understood at all, it is clear that any transport model, however complex in its mathematics, is a gross simplification of actual processes.

With this understanding at hand, we proceed and state, equivalent to (4) for liquid flow, the classical equation that is thought to describe one-dimensional solute transport during transient flow

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \theta c}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z} - qc\right) + \sum_i \phi_i(c, s, \cdots) \qquad (10)$$

where c and s are solute concentrations associated with the solution and solid phases of the soil, ρ is the soil bulk density, D is the dispersion coefficient, q is the soil water flux density, and ϕ_i are rates of solute removal or supply not specifically included in s. Although (10) is the cornerstone of most theoret-

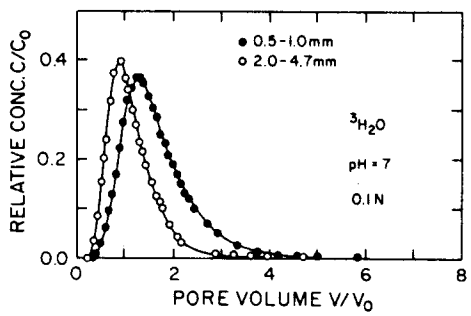

Fig. 15. Observed ^3H_2O effluent curves showing the effect of aggregate size on the displacement process.

ical descriptions of solute transport, its form is tentative in several respects, notably with regard to the proper definitions of D, s, and ϕ_i as will be discussed below. The equation is also fraught with uncertainties of applicable temporal [*Skopp*, 1986] and spatial scales [*Dagan*, this issue] that are not easily resolved.

In practice, D is used as an empirical parameter that includes all of the solute spreading mechanisms that are not directly included in (10) through the definitions on s and ϕ_i, such as nonlinear adsorption or exchange, nonlinear decay, or various physical and chemical nonequilibrium conditions. In concept, however, the coefficient is commonly assumed to reflect two additive phenomena: ionic or molecular diffusion arising from the natural thermal motion of dissolved constituents, and mechanical dispersion resulting from the fact that local fluid velocities inside individual pores and between pores of different shapes, sizes and directions, deviate from the average fluid flux. Because the inter- and intraaggregate concentration and pore water velocity distributions depend on geometric configurations of the pores as well as on the concentration and ionic composition of the soil solution, previously established relationships between D and macroscopically observable parameters must be considered to be strictly empirical. Also, since diffusion is an active process in response to concentration gradients irrespective of flow while dispersion is a passive process in response to fluid flow, the additivity of the two processes must be questioned. Nevertheless, the dispersion coefficient so defined in a one-dimensional system attains the form

$$D = D_0\tau + \lambda|v|^n \tag{11}$$

where D_0 is the diffusion coefficient, τ is a tortuosity factor that likely depends on the water content [*Kemper and van Schaik*, 1966] but not on the pore water velocity v, and where λ and n are empirical constants. For relatively homogeneous, saturated systems, the exponent n has been shown to be approximately unity [*Saffman*, 1959], and hence λ has since become known as the dispersivity. The value of λ typically ranges from about 0.005 m or less for laboratory scale experiments involving disturbed soils, to about 0.1 m or more for field scale experiments [*Biggar and Nielsen*, 1976; *Van de Pol*, 1977; *Jury and Sposito*, 1985]. Recent studies also suggest a dependency of λ on the spatial scale of the experiment, as well as on prevailing vertical and areal heterogeneities of field soils [*Anderson*, 1979; *Dagan*, this issue].

The first term of (10) describes the rate at which the solute interacts or exchanges with the solid phase. Its exact form [*Helfferich*, 1962] continues to be heavily debated. A resolution of this debate usually rests on the consistency between the scale at which the phenomenon is perceived and the scale of the observation at which the perceptions are tested; see *Skopp* [1986] for an excellent discussion of this issue. Both equilibrium and kinetic rate laws have been used to describe the adsorption-exchange process (see sections 6.1 and 6.2, respectively). Often, the sorption term also depends significantly on more than one solute species, thus requiring the inclusion of appropriate solution chemistry and/or cation exchange submodels. Several distinctly different modeling techniques can be used for such multicomponent systems. One approach is to insert all of the interaction chemistry directly into the transport equations and thus to reduce the problem to a set of coupled nonlinear partial differential equations of the form of (10) [*Rubin and James*, 1973; *Valocchi et al.*, 1981; *Jennings et al.*, 1982]. Although this approach can lead to accurate results, the method is generally expensive except for situations where only a limited number of solute species is involved. Computationally more efficient methods arise when some or all of the solution and exchange chemistry is formulated independently of the mass transport equation. This approach leads to a set of nonlinear algebraic equations for the solution and exchange chemistry and one or only a few differential equations for the transport part of the model. Examples of the latter approach, in various degrees of complexity, are given by *Schulz and Reardon* [1983], *Miller and Benson* [1983], and *Cederberg et al.* [1985].

The last term ϕ_i in (10) accounts for sources and sinks in the system, most of them being irreversible during the time period over which the equation is considered. The most commonly modeled processes are those of radioactive decay, chemical precipitation and dissolution, absorption of solutes by the plant roots, and the utilization and transformation of solutes by soil microorganisms. The weathering of clays, the decomposition of soil minerals, and oxidation-reduction reactions have also been considered. Except for radioactive decay, the terms ϕ_i for the above processes are somewhat ambiguous and apply more or less to local conditions since their behavior depends on complex interrelationships of many environmental and biological parameters incapable of being modeled without several empirical relationships and many simultaneous equations that are not amenable to simple solutions.

The same is true for the growth and decomposition of plant roots and their attendant absorption or release of solutes in the soil profile. The term ϕ_i for these processes is perhaps the most difficult to model. The major difficulty describing plant root absorption, even after all environmental parameters are conceptually included, is that the scale of root growth is at least one order of magnitude greater than the scale of the dimensions applicable to (10).

With the above discussions related to (10), it is easily understood that many combinations of terms, ionic species, and auxiliary conditions specifying various initial and boundary conditions exist to describe transport processes in the vadose zone. In the next few sections we will discuss several specific transport models that represent various simplifications of the overall physicochemical transport problem at the microscopic level.

6. Solute Transport Models

While transport under field conditions generally requires the simultaneous solution of the unsaturated flow (equation (4)) and transport (equation (10)) equations, we restrict ourselves here to simplifications of (8) for steady flow at constant water contents. Numerical solutions of the combined unsaturated flow and transport equations have been presented in various publications, both for one-dimensional (*Bresler and Hanks* [1969]; *Bresler* [1973]; *Kirda et al.* [1973]; *Wood and Davidson* [1975]; *Ungs et al.* [1976]; *van Genuchten* [1981*a*]; among others) and multidimensional problems (*Duguid and Reeves* [1976]; *Segol* [1977]; *Pickens and Gillham* [1980]; *Yeh and Ward* [1981]; *Gureghian* [1983]; *Huyakorn et al.* [1985]; among others). Of significance here is a study by *Wierenga* [1977], who showed that an average pore water velocity used as a constant in (8) could be used effectively instead of the more complicated transient description. This suggests that the simpler models based on steady state flow can at times provide realistic predictions in the field. This may be especially true if one is primarily interested in long-term rates and

amounts of solute leaving the upper part of the vadose zone (e.g., the crop root zone), thus neglecting short-term and highly dynamic oscillations near the soil surface.

6.1. *Equilibrium Transport*

Adsorption or exchange reactions perceived as instantaneous are described by equilibrium isotherms $s(c)$, which can be of the mass action, linear, Freundlich, or Langmuir type, or of many other functional forms [*Bolt*, 1979; *Travis and Etnier*, 1981]. In soil studies it has been shown that these isotherms, as well as generally being limited to narrow ranges in concentration, sometimes can take on different values for adsorption as compared with desorption, especially for organic solutes [*Swanson and Dutt*, 1973; *van Genuchten et al.*, 1974].

The most common approach for modeling the sorption term has been to assume instantaneous adsorption or exchange, as well as simple linearity between s and c as follows:

$$s = kc \tag{12}$$

where k is the slope of the isotherm $s(c)$, often referred to as the distribution coefficient K_d. While the simplicity of (12) is a convenient feature for mathematical modeling purposes, its limitations should be clearly understood inasmuch as adsorption and exchange processes usually are nonlinear and also depend on the presence of competing species in the soil system. For helpful discussions of this problem, see *Reardon* [1981], *Miller and Benson* [1983], and *Valocchi* [1984].

To also arrive at a relatively simple form for the source-sink term in (10), ϕ_i is often approximated by first- and/or zero-order rate terms:

$$\phi_i = -\mu_l\theta c - \mu_s\rho s + \gamma_l\theta + \gamma_s\rho \tag{13}$$

where μ_l and μ_s are rate constants for first-order decay in the liquid and adsorbed phases, respectively, and where γ_l and γ_s are similar zero-order production terms for the two phases. For radioactive decay, one may safely assume that the first-order rate coefficients μ_l and μ_s are identical, as well as neglect the zero-order processes. For chemical or microbiological degradation, however, all rate coefficients are likely to have different values. Substituting (12) and (13) into (10) and assuming steady state flow, the transport equation simplifies to the classical linear convection-dispersion equation

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial x} - \mu c + \gamma \tag{14}$$

where the retardation factor R is given by

$$R = 1 + \rho k/\theta \tag{15}$$

and with the new rate coefficients μ and γ

$$\mu = \mu_l + \mu_s\rho k/\theta \tag{16a}$$

$$\gamma = \gamma_l + \gamma_s\rho/\theta \tag{16b}$$

Equation (14), with or without the adsorption and/or the decay terms, has been solved for a large number of initial and boundary conditions for both finite and semi-infinite systems [*van Genuchten and Alves*, 1982; *Javandel et al.*, 1984]. Similar solutions also exist for the multidimensional forms of (14); these solutions generally hold only for unidirectional flow [*Cleary and Ungs*, 1978; *Carnahan and Remer*, 1984].

Transport equation (14) needs to be modified when organic or inorganic decay products become of interest. The simplest case arises when the decay products form a consecutive decay chain. Ignoring zero-order terms, the system of partial differential equations becomes

$$R_1\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - v\frac{\partial c_1}{\partial z} - \mu_1 c_1 \tag{17a}$$

$$R_i\frac{\partial c_i}{\partial t} = D\frac{\partial^2 c_i}{\partial z^2} - v\frac{\partial c_i}{\partial z} + \mu_{i-1}c_{i-1} - \mu_i c_i \qquad i \geq 2 \tag{17b}$$

where i is the number of species considered in the decay chain. Equations (17*a*) and (17*b*) are standard expressions for radioactive decay [*Lester et al.*, 1975; *Rogers*, 1978; *Harada et al.*, 1980; *Gureghian and Jansen*, 1983]. In soil studies, the equations have been applied to consecutive decay chains of nitrogen species [*Cho*, 1971; *Misra et al.*, 1974; *Starr et al.*, 1974; *Wagenet et al.*, 1976], organic phosphates [*Castro and Rolston*, 1977], and pesticides [*Bromilow and Leistra*, 1980].

Application of (17*a*) and (17*b*) to microbially induced organic and inorganic transformations in concept should include provisions for the growth and maintenance metabolisms of soil microbes. Proper definition of the source-sink term ϕ_i for such situations remains problematic. *McLaren* [1970] provided a useful review of temporal and vectorial reactions of soil nitrogen in which it is made abundantly clear the microbial growth and maintenance as well as waste metabolisms must be considered as functions of both time and space in soil systems; similar considerations apply also to biotransformations of organic compounds [*Blanch*, 1981; *McCarty et al.*, 1984]. McLaren's analysis of ϕ_i leads to

$$\phi_i \equiv \frac{\partial S}{\partial t} = -A\frac{\partial m}{\partial t} - Bm - \frac{\kappa\delta mS}{\kappa_m + S} \tag{18}$$

where S is the substrate concentration, m is the biomass, A is a constant equal to the reciprocal of the growth yield, B is the maintenance coefficient, κ is a constant, δ is the amount of enzyme per unit biomass, and κ_m is a saturation constant. For very small substrate concentrations, where $\partial m/\partial t = \varepsilon m$ and $\kappa_m \gg S$, (18) reduces to the first-order reaction

$$\partial S/\partial t = -(A\varepsilon + B)m - \kappa\delta mS/\kappa_m \tag{19}$$

The above equations are convenient, but not necessarily correct when applied to soil systems. For example, the biomass m is a lumped term for all microbiological species, each of which has its own metabolic parameters and each of which may be antagonistic or synergystic to other species. It should also be recognized that the use of the term substrate is categorically different than a particular solute believed to be the rate-limiting nutrient constituent of the substrate. The utility of (18) and (19), as well as of similar formulations applied to field conditions, hinges on an analysis of their parameter values specifically measured for the local environmental conditions as a function of time and space. In any event, it should be clear that (17*a*) and (17*b*) are only approximate, with real systems being far more complicated. For examples of the level of complexity that has been attained with more elaborate models, see *Frissel and van Veen* [1980] and *Iskandar* [1981]. These studies amply show that our current knowledge of the physical and chemical properties of soils far exceeds that of microbially induced transformations during leaching. Thus additional research in this area is sorely needed.

Application of (14) to transport through disturbed soil columns in the laboratory and in relatively uniform field soils involving nonreactive or only weakly reactive solutes has been fairly successful. Unfortunately, the equation has not per-

formed well in several situations, especially for strongly adsorbed chemicals (large k) and for naturally aggregated soil systems. The main reason for this failure is the likelihood that chemical transport is not at equilibrium. Various chemical-kinetic and diffusion-limited rate laws have consequently been proposed to describe this nonequilibrium transport. These are discussed next.

6.2. *Nonequilibrium Transport*

Diffusion-controlled or chemically controlled kinetic rate reactions, or both, of the form $\partial s/\partial t = f(s, c)$ have been examined from various viewpoints. The most popular and simplest formulation arises when first-order linear kinetics is assumed. Ignoring the degradation terms, (14) is replaced by the coupled system

$$\frac{\rho}{\theta}\frac{\partial s}{\partial t} + \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} \tag{20a}$$

$$\frac{\partial s}{\partial t} = \alpha(kc - s) \tag{20b}$$

where α is a first-order rate coefficient. Although (20*a*) and (20*b*) or similar rate models have resulted in some improvements in predictive capabilities, notably for miscible displacement experiments in the laboratory, success has generally been limited to experiments conducted at relatively low pore water velocities [*Davidson and McDougal*, 1973; *Hornsby and Davidson*, 1973; *van Genuchten et al.*, 1974]. Various alternative equations and transport models have thus been developed to account for observed deviations.

Lindstrom and Boersma [1970] suggested a physically more meaningful expression inasmuch as it accounts for the quantum-mechanical features of changing potentials or energies of activation with changing surface coverage. Their rate model allows the realistic property of the potential for adsorption to be greatest in regions of initially small chemical concentrations. Unfortunately, the equation did not materially improve transport predictions in at least one comparison with other kinetic models [*van Genuchten et al.*, 1974]. *Akratanakul et al.* [1983] recently proposed an alternative equation that considers the adsorption process as a three-step mechanism consisting of diffusion from the bulk solution to a liquid film around the soil particles, constant-rate diffusion across the liquid film, and a kinetic surface reaction.

An attractive chemical nonequilibrium model that did lead to improved transport descriptions is the two-site model where the adsorption term is thought to consist of two components, one governed by equilibrium adsorption, and one by first-order kinetics [*Selim et al.*, 1976; *Cameron and Klute*, 1977]. Basic to this model is the idea that the solid phase of the soil is made up of various constituents (soil minerals, organic matter, iron and aluminum oxides) and that a chemical is likely to react with these constituents at different rates and with different intensities. The model assumes that the sorption/exchange sites can be divided into two fractions: adsorption on one fraction ("type-1" sites) is assumed to be instantaneous, while adsorption on the other fraction ("type-2" sites) is assumed to be time-dependent. This leads to the following formulation [*Nkedi-Kizza et al.*, 1984]:

$$\left(1 + \frac{F\rho k}{\theta}\right)\frac{\partial c}{\partial t} + \frac{\rho}{\theta}\frac{\partial s_2}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} \tag{21a}$$

$$\frac{\partial s_2}{\partial t} = \alpha[(1 - F)kc - s_2] \tag{21b}$$

where F is the mass fraction of all sites being occupied with type-1 equilibrium sites, and where the subscript 2 refers to type-2 sites. While limited to laboratory displacement experiments, the two-site model was successfully used to describe the transport of various organic and inorganic chemicals [*Cameron and Klute*, 1977, *DeCamargo et al.*, 1979; *Rao et al.*, 1979; *Hoffman and Rolston*, 1980; *Nkedi-Kizza et al.*, 1983]. Unfortunately, the parameters F and α in most studies were found to be functions of the pore water velocity and could generally not be derived independently from batch equilibrium studies. They usually needed to be adjusted for different experiments carried out on the same soil columns, thus suggesting that other than linear first-order kinetic processes dominate the sorption process during water movement.

Nonequilibrium conditions have also been explained by assuming diffusion controlled sorption. Because of relatively small particles and because of vigorous shaking, diffusion can generally be eliminated as a rate-limiting step in batch-type kinetic and equilibrium studies [*Helfferich*, 1962]. This situation does not occur in soils with flowing water, where the sorption rate may be limited by the rate at which the ions are transported by diffusion to the exchange sites. This alternative conceptualization has resulted in "physical nonequilibrium" models that partition soil water in mobile (flowing) and stagnant (immobile or nonmoving) phases. The approach in effect assumes that the pore-water velocity distribution is bimodal: convective-dispersive transport is confined to only a fraction of the liquid-filled pores, while the remainder of the pores have stagnant water. This stagnant water has been visualized as thin liquid films around soil particles, as dead-end pores [*Coats and Smith*, 1964], as nonmoving intraaggregate water [*Philip*, 1968; *Passioura*, 1971], or as relatively isolated regions associated with unsaturated flow [*Nielsen and Biggar*, 1961]. Transport models based on first-order exchange of solute between mobile and stagnant regions were initially discussed in the petroleum and chemical engineering literature for nonadsorbing chemicals [*Coats and Smith*, 1964; *Villermaux and van Swaay*, 1969]. *Van Genuchten and Wierenga* [1976] extended the above concepts of mobile-immobile water to include Freundlich-type equilibrium adsorption-desorption processes. Their equations are of the form

$$\theta_m R_m\frac{\partial c_m}{\partial t} + \theta_{im}R_{im}\frac{\partial c_{im}}{\partial t} = \theta_m D_m\frac{\partial^2 c_m}{\partial z^2} - \theta_m v_m\frac{\partial c_m}{\partial z} \tag{22a}$$

$$\theta_{im}R_{im}\frac{\partial c_{im}}{\partial t} = \alpha(c_m - c_{im}) \tag{22b}$$

where the subscripts m and im refer to mobile and immobile regions, respectively, and α is a mass transfer coefficient, interpreted as a diffusion coefficient divided by some average diffusional path length. The retardation factors R_m and R_{im} account for equilibrium type adsorption processes in the mobile and immobile regions, respectively.

The applicability of (22*a*) and (22*b*) for a variety of tracers (tritiated water, chloride, organics, heavy metals) to laboratory scale transport processes has been clearly demonstrated [*Gaudet et al.*, 1977; *Bolt*, 1979; *Nkedi-Kizza et al.*, 1983]. As an example, Figure 16 shows observed and calculated effluent curves for boron movement through a 30-cm-long unsaturated soil column filled with relatively small aggregates (less than

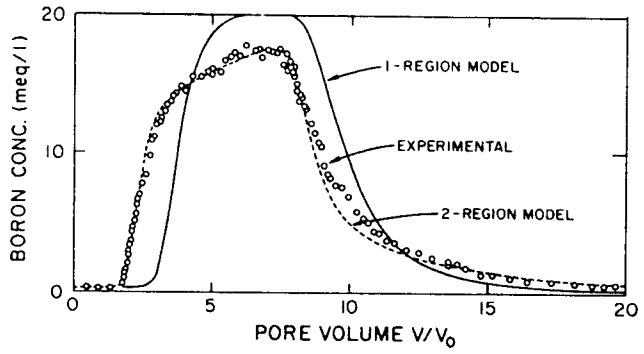

Fig. 16. Observed and calculated boron effluent curves from an aggregated clay loam soil column.

0.63 mm in diameter) of a calcareous Glendale clay loam soil. The dashed curve was obtained with (22*a*), (22*b*) and the solid curve with (14), both models being modified to include a nonlinear Freundlich-type equilibrium isotherm measured at the *p*H of the displacement experiment. Pertinent parameter values are given elsewhere [*van Genuchten*, 1981*b*]. Figure 16 clearly shows an accelerated movement of the boron tracer pulse through the soil and an associated tailing phenomenon process (asymmetry) at higher pore volumes. In this example, tailing is caused in part by an apparently modest amount of stagnant water (estimated to be about 15% of the total water), and in part by the fact that about 45% of the sorption sites are estimated to be located inside the aggregates away from the larger fluid-filled pores. Adsorption-exchange inside aggregates is an important and often overlooked phenomenon in transport studies involving reactive tracers. Sorption and exchange sites are often not located along the main fluid flow lines, but along dead-end pores, or inside clusters of particles or aggregates that have larger internal surface areas. Even with a small amount of stagnant water in the system, an uneven distribution of sorption sites can lead to significant "preferential transport" and hence asymmetry and tailing when strongly adsorbed solutes (heavy metals, radionuclides) are present.

Comparison of the two-site (equations (21*a*) and (21*b*)) and physical nonequilibrium "two-region" (equations (22*a*) and (22*b*)) models shows that they have the same mathematical structure and can be put in the same dimensionless form by means of model-specific dimensionless parameters. *Nkedi-Kizza et al.* [1984] used this information to show that effluent curves from laboratory soil columns alone cannot be used to differentiate between the specific physical and chemical phenomena that cause an apparent nonequilibrium situation in a soil. This means that independent parameter estimates are needed for verification of the two phenomena. The similarity of the two transport models also means that the two formulations can be used in a macroscopic and semiempirical manner without having to delineate the exact physical and chemical processes on the microscopic level. A rigorous analysis of diffusion of ionic species to less accessible sites should have been described by Fick's second law of diffusion. This may be possible if the shapes and sizes of aggregates are exactly known, as is the case for geometrically well-defined aggregated systems. However, this is not easily done for soils that contain irregularly shaped, small-sized aggregates, and ironically also not for seemingly homogeneous soils. Because of the fuzzy geometric distribution of immobile water pockets and associated sorption sites, several parameters in (22*a*) and (22*b*), notably α and to some extent also θ_m, often must be fitted to observed data before the model can be used. While accurate optimization programs are available for that purpose [*van Genuchten*, 1981*b*; *Parker and van Genuchten*, 1984], their use accentuates the semiempirical nature of present models. It also demonstrates that the nonequilibrium transport problem, at least at the microscopic level, remains largely unsolved.

6.3. *Transport in Structured Soils*

The above geometric limitations at the microscopic level can be relaxed somewhat when simulating transport in soils that contain well-defined macropores or that are made up of relatively large, uniformly sized and shaped aggregates. A large number of analytical two-region or "bicontinuum" models are presently available for such structured (or fractured) systems. A commonality of these models is the assumption that the chemical is transported through a single, well-defined pore or crack of known geometry, or through the voids between well-defined, uniformly sized aggregates. In addition, diffusion-type equations are used to describe the transfer of solute from the larger pores into the micropores of the soil matrix. For example, for uniformly sized spherical aggregates of radius a, (22*a*) remains valid for the transport in the macropore (mobile) phase, while (22*b*) must be replaced by the spherical diffusion equation

$$R_{im}\frac{\partial c_a}{\partial t}=\frac{D_a}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_a}{\partial r}\right)\qquad 0\le r\le a \tag{23}$$

where $c_a(z, r, t)$ is the local concentration in the spherical aggregate; r is the radial coordinate; and D_a is the effective porous matrix diffusion coefficient ($D_0\tau$). The average immobile concentration c_{im} in (22*a*) is now the average concentration of the intraaggregate liquid phase:

$$c_{im}(z, t)=\frac{3}{a^3}\int_0^a r^2 c_a(z, r, t)\,dr \tag{24}$$

Several analytical [*Rasmuson and Neretnieks*, 1980] and numerical solutions [*Rao et al.*, 1980; *Huyakorn et al.*, 1983] of the above spherical diffusion transport model, with and without first-order decay, have been derived. Similar analytical solutions also exist for transport through rectangular voids [*Sudicky and Frind*, 1982] and hollow cylindrical macropores [*van Genuchten*, 1985], and for transport around solid cylindrical structures [*Pellett*, 1966]. In addition, relatively simple solutions are available that neglect solute dispersion in the macropores [*Skopp and Warrick*, 1974] or that assume matrix diffusion into aggregates of infinite dimensions [*Tang et al.*, 1981; *Grisak and Pickens*, 1981]. Application of those solutions to laboratory-scale experiments involving both disturbed and undisturbed soil columns has been quite successful [*Rao et al.*, 1980; *Nkedi-Kizza et al.*, 1982; *Grisak and Pickens*, 1981]. As an example, Figure 17 shows calculated and experimental curves for ^{45}Ca transport through an aggregated oxisol at two pore water velocities. Calculated curves in this case were based on a numerical solution of the spherical diffusion model; pertinent parameter values are given by *Nkedi-Kizza et al.* [1982]. A recent application of the spherical diffusion model to in situ field data involving chloride and two organic tracers is described by *Goltz and Roberts* [1986].

The above modeling procedures have been restricted to uniformly sized and shaped aggregates of specific geometry. The natural variability of aggregate geometries in the vadose zone requires a generalization of the two-region approach to other aggregate shapes, as well as to mixtures of aggregates having

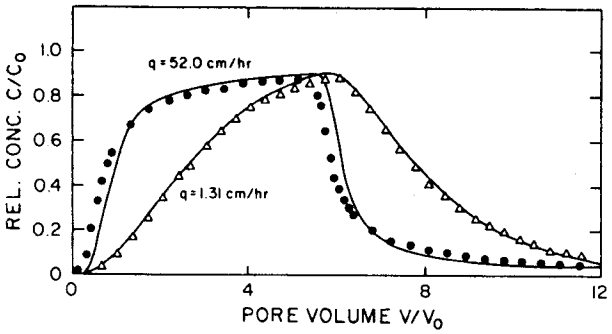

Fig. 17. Observed and calculated ^{45}Ca effluent curves from an aggregated oxisol at two different flow rates [after *Nkedi-Kizza et al.*, 1982].

different shapes and sizes; recently, several papers have attempted to do so [*Rao et al.*, 1982; *Barker*, 1985; *Rasmuson and Neretnieks*, 1984].

Although the above two-region modeling approach is conceptually pleasing and has resulted in improved prediction capabilities, the question still arises whether a geometry-inspired model is too complicated for routine use. By its very nature, a geometry-based model allows exact solutions only for simple systems (input parameters generally must be constant in time and space), and for highly simplified initial and boundary conditions. They also require a large number of parameters that are not easily measured independently. In contrast, the classical Fickian-based transport equation is much simpler and thus more suited for practical field applications. Moreover, the classical model may well be applicable to certain limiting conditions dictated by the spatial scale of the transport problem, the aggregate size and the pore water velocity. Thus, several attempts have been made to define conditions at which the classical model may be valid [*Valocchi*, 1985; *Parker and Valocchi*, 1986], in which case the effects of intraaggregate diffusion can be lumped into an effective dispersion coefficient for use in (14). For example, for uniformly sized spherical aggregates of radius a, the effective dispersion coefficient D becomes [*Parker and Valocchi*, 1986]

$$D = D_m\phi_m + \frac{(1-\phi_m)a^2v^2R_{im}}{15D_aR^2} \qquad \phi_m = \theta_m/\theta \qquad (25)$$

which is a simple variant of similar expressions derived previously by *Passiouira* [1971] and *Bolt* [1979] for the nonreactive case. The form of (25) suggests that simple linearity between D and v (equation (11)) with $n = 1$) may not hold for structured soils.

Similar equations have also been derived that relate the empirical mass transfer coefficient α in (22*a*) and (22*b*) to measurable soil physical parameters, notably aggregate size, diffusion coefficient, and pore water velocity. From these studies [e.g., *van Genuchten*, 1985] it has become evident that the first-order mobile-immobile transport model works well for hollow cylindrical macropore systems, with predictions for spherical and other aggregate geometries being far less accurate.

6.4. *Organic Transport*

The transport of organic solutes in soil has recently received increasing attention even though the movement of naturally occurring organics has long been recognized. The impetus of this attention results from the adverse impact of toxic organic chemicals on the environment when released at hazardous levels and from the objective to effectively and safely use certain classes of compounds for the control of pests. Some of the same concepts and models previously mentioned have been utilized to describe the behavior of organic compounds which do not occur naturally in the environment (for recent review of organic transport and its modeling, see *MacKay et al.* [1985] and *Wagenet and Rao* [1985]). At the same time it must be recognized that certain characteristics of these compounds require additional attention. The molecular size, structure, polar characteristics, as well as the presence of several charged and uncharged functional groups on the molecule, lead to a wide range in solubility in both aqueous and natural organic phases in the soil.

Additional properties such as volatility, immiscibility, and hydrophobicity may complicate the description of processes and need to be included in the transport equations previously described. While not explicitly mentioned, the emphasis there was placed on processes of miscible displacement (with the exception of two-phase air-liquid flow; section 4.3), whereas the transport of some organics may be more closely related to multiphase immiscible displacement [*Dullien*, 1979; *Marle*, 1981]. In particular situations, often found in chemical disposal areas, a complete mixture involving several different organic chemicals with different miscibilities in both aqueous and nonaqueous phases exists. Models developed to predict the movement of such chemicals through the vadose zone might therefore need to include the descriptions of volatilization, adsorption-desorption, microbial, chemical and photochemical transformations, and miscible and immiscible characteristics. The sophistication of such models will depend upon the objective the model is to address. For example, *Jury et al.* [1983, 1984] developed a useful analytical model to screen or group compounds as to their potential hazard for groundwater contamination. Such a screening model can be far less complex than those required for prediction of the temporal and spatial exposure of pests to the chemical or for prediction of the residence time in the vadose zone [e.g., *Abriola and Pinder*, 1985; *Faust*, 1985]. It could be argued on the one hand that considerable progress has been made in the description of the transport of organics in unsaturated soil since their large-scale utilization and disposal less than three decades ago. On the other hand, progress in theoretical and experimental developments relative to this group of compounds is no further advanced than any other group of compounds discussed in this paper.

7. CONCLUDING REMARKS

In this review we attempted to illustrate the tremendous effort that has been directed toward unravelling the interactive physical, chemical, and microbiological mysteries of flow and transport processes in the unsaturated zone. The effort has, in an exponential way, increased our conceptual understanding of the major mechanisms affecting flow and transport, perhaps to the point of frustration when realizing the complexity of the transport problem. Hydrologists, soil scientists, geochemists, microbiologists, and others all have contributed in small or large pieces. Still, tremendous opportunities for research remain, as is the urgency for progress as our soil and groundwater resources are increasingly subjected to the dangers of long-term pollution.

We concentrated primarily on conceptual aspects of various deterministic-mathematical approaches for modeling flow and transport in the unsaturated zone. Various stochastic and statistical approaches geared toward field scale variability and

heterogeneity are discussed by *Dagan* [this issue]. Eventually, both approaches must be integrated to effectively deal with field scale flow and transport. Moreover, without adequate experimental verification, none are likely to be safely employed.

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J. W. Biggar and D. R. Nielsen, Department of Land, Air, and Water Resources, University of California, Davis, CA 95616.

M. Th. van Genuchten, U.S. Salinity Laboratory, U.S. Department of Agriculture, Agricultural Research Service, 4500 Glenwood Drive, Riverdale, CA 92501.

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