New Issues and Challenges in Soil Physics Research

M. *Th. van Genuchten*

Volume 1: Inaugural and State of the Art Conferences

pp. 5-27

Transactions, 15th World Congress of Soil Science, Acapulco, Mexico

July 10-16, 1994

Published by the International Society of Soil Science
and the Mexican Society of Soil Science

New Issues and Challenges in Soil Physics Research

M. Th. van Genuchten. U.S. *Salinity Laboratory, USDA, ARS, 4500 Glenwood Drive, Riverside, CA, 92501, USA.*

Abstract. The focus of soil physics research, and that of soil science in general, has gradually broadened from mostly agricultural production issues to more comprehensive studies of subsurface water flow and chemical transport geared toward environmental issues. There is an abundance of ongoing and new challenges in soil physics research, notably in the areas of subsurface heterogeneity (including preferential flow), multiphase flow, multicomponent transport, and hydraulic property characterization. Soil heterogeneity at a variety of spatial scales remains a frustrating problem affecting the measurement, prediction, and management of subsurface flow and transport processes. More realistic deterministic and stochastic models, as well as improved sampling methods and instrumental techniques, are slowly becoming available to make the research more effective. Several examples are given to illustrate soil physics contributions to the solution of agricultural and environmental problems.

Introduction

Much evidence exists of increased human-induced stresses on the earth's environment. Many of these stresses are, directly or indirectly, a consequence of pollutants generated by agricultural, industrial, and municipal activities. Pesticides and fertilizers used in farming operations continue to contaminate soil and groundwater systems worldwide. Soil erosion remains a problem in many areas. The accumulation of salts and toxic elements in irrigation agriculture is a worsening problem in many arid and semi-arid regions of the world. Acid rain is a cause of pollution in most or all continents. Chemicals migrating from municipal and industrial disposal sites are similarly creating hazards to the environment. Especially challenging are nonaqueous phase liquids including chlorinated hydrocarbons, polychlorinated biphenyls and related toxic substances. Radionuclides released into the environment (including those produced by the Chernobyl disaster) are also increasingly becoming a problem. The much-debated topics of deforestation, biodiversity, and climatic change, are real and must be of concern to all of us.

Contamination of the subsurface poses special challenges to soil scientists including soil physicists. Many or most subsurface pollution problems stem directly from activities involving the unsaturated (vadose) zone between the soil surface and the groundwater table. It is the unsaturated zone where management will offer the best opportunities for preventing or limiting pollution, or for remediating ongoing pollution problems. Solute residence times in groundwater aquifers can range from several years to millennia or more. Hence, once contaminants have entered groundwater, pollution is in many cases essentially irreversible, or can be remediated only with extreme costs. Consequently, soil and groundwater pollution problems are best dealt with, or prevented, through proper management of the unsaturated zone. Because of our expertise in the measurement and modeling of unsaturated zone flow and transport processes, soil physicists are in a unique position, and have special responsibilities, to contribute to the prevention or remediation of subsurface pollution problems.

This paper addresses some of the opportunities for soil physicists in the continuing effort to optimize agricultural production, while also contributing to the solution of environmental problems. It is critical that our research be part of comprehensive efforts involving other soil scientists, hydrologists, geologists, civil and environmental engineers, and (micro)climatologists. In this paper I shall concentrate mostly on flow and transport processes in the unsaturated zone. Areas of research where progress has been obtained, or where progress is particularly needed, will be emphasized. These areas include, but are not limited to, flow through deep unsaturated soil profiles, preferential flow, flow and transport in unsaturated fractured rock, multiphase flow, better methods and instrumentation for measuring model parameters, the need to improve communication between soil scientists globally, and the educational implications of a broader soil physics perspective.

Soil, Physics, and Soil Physics

Soil physics may be defined as the application of the principles of physics to the characterization of soil properties and the understanding of soil processes, especially those involving the transport of matter or energy (Sposito and Reginato, 1992). This definition implies that soil physics is a subdiscipline of both physics and soil science. While useful, the definition does not necessarily reflect the type of research typically carried out by soil physicists. It may be instructive to briefly consider typical research topics dealt with by soil physicists over the past several decades.

Early studies of soil physics from the 1900s to the 1940s generally involved such issues as soil structure and soil aggregation, soil pore space, field soil water status, capillarity and soil water retention, evaporation, soil mechanics, soluble salts, soil salinity, diffusion, and heat content. Many of these early studies focused on the physical properties of soils as a medium for crop production, including the effects of tillage and compaction on root growth and plant water uptake. More comprehensive theoretical studies by soil physicists on water, heat and solute movement in soils started in the 1930s with the formulation of the Richards equation for transient unsaturated- water flow (Richards, 1931). Similar differential equations were introduced for heat and solute movement, and subsequently applied in the 1950s and 1960s to a flurry of laboratory experiments involving mostly disturbed, homogeneous soil systems. Laboratory testing of convection-dispersion type solute transport models was especially popular at that time. Field-scale testing of flow/transport theories and models did not really start until the mid 1970s in part spurred by the development of better numerical models and the increased availability of mainframe and personal computers. Process-based simulation models were subsequently developed for the purpose of integrating available knowledge, and for formulating and evaluating alternative agricultural soil, crop, and water management practices. While most of these simulations initially focused primarily on water quantity issues (irrigation, drainage, soil erosion), they increasingly also involved agricultural water quality issues associated with pesticides, fertilizers, soil salinity, and sewage sludge.

Soil physicists must remain concerned about the physical environment of plants. Agricultural production unquestionably will remain a critical issue as the world’s population keeps increasing in an era of limited soil and water supplies. At the same time, however, soil scientists/physicists have also a responsibility to address soil and groundwater pollution problems caused by agricultural and non-agricultural sources at local, regional, and global scales. It is critical that these environmental problems be addressed in a systematic manner involving efforts which cross disciplinary, institutional, and geographic barriers. The need for a broad multidisciplinary perspective should be obvious in view of the many physical, chemical and biological processes known to affect the behavior and transport of water and dissolved constituents in the subsurface environment. The following examples illustrate the need for a more broadly defined framework of soil physics research.

First, soil physics research can no longer be confined to the upper soil horizons between the soil surface and a depth of 2 m traditionally viewed as the lower boundary of the soil medium (e.g., the bottom of the root zone). Soil physicists must be concerned with flow and transport processes in the entire vadose zone between the soil surface and the groundwater table, even if the vadose zone is hundreds of meters deep as is often the case in arid and semi-arid areas. We must be able to quantify how flow and transport processes in the vadose zone affect the quality of underlying or down-gradient groundwater reservoirs. In situations involving shallow water tables, we must be concerned not only with downward flow and transport, but conversely also with possible upward flow of water and dissolved constituents. Because of the dangers of (secondary) soil salinization, shallow water table management is a special concern in arid and semi-arid regions. An integrated soil/aquifer research approach requires interaction with hydrologists and geologists.

Second, soil physicists are increasingly becoming participants in global-scale hydrologic research. Especially needed (e.g., Wood, 1991) are improved models of land-surface hydrologic processes in general circulation models for predictions at regional, continental, and global scales, as well as appropriate field studies over a range of scales insofar as these scales impact hydrological processes at the larger scales. Soil physicists should be especially interested in the land surface component of global hydrological models, including the development of realistic physically-based models for biosphere-atmosphere interactions to estimate the transfer of energy, mass, and momentum between the vegetated surface of the earth and the atmosphere.- With their traditional focus on soil water dynamics and microclimatology, soil physicists should be natural cooperators in research with hydrologists, climatologists and global climate modelers.

Third, soil physicists must be interested in media other than the weathered and fragmented outer layer of the earth's terrestrial surface usually referred to as *soil (e.g.,* Hillel, 1980). Development of realistic models for unsaturated flow and solute transport in fractured rock and other geologic materials is crucial for establishing suitable subsurface waste disposal sites. For example, much research in several countries has been, or is being, carried out in connection with the safe disposal of spent nuclear fuel and high-level radioactive waste in unsaturated fractured rock (e.g., Evans and Nicholson, 1987). The same is true for the performance of clay liners as barriers to the migration of contaminants from waste disposal sites. Soil physicists can, and should, provide much expertise to these projects.

Fourth, soil physicists must be concerned with fluids other than water, which traditionally has been the main focus in agricultural research. For example, subsurface pollution by nonaqueous phase liquids (NAPL's) is increasingly becoming a problem in many countries. While multiphase (air-water-oil) fluid systems pose additional problems, soil physicists have long worked almost exclusively on the measurement and modeling of two-phase air-water systems; they must provide sorely needed input into multiphase flow research. Soil physicists have made, and should continue to make, important contributions to theoretical studies of NAPL transport, including the measurement and scaling of multiphase capillary-pressure saturation and permeability relationships. The same is true for vapor phase transport involving volatile organic chemicals and other constituents.

Fifth, soil physicists must be equally concerned with agricultural chemicals (fertilizers, pesticides, soil salinity) as well as with nonagricultural chemicals, including radionuclides, toxic trace elements, and certain volatile organics. Colloid-facilitated contaminant transport should similarly be a concern to soil physicists.

The above examples demonstrate that soil physicists are or should be involved in a broad array of research topics well beyond the traditional boundaries of soil physics. In the remainder of this paper I will address a few selected topics on flow and transport in the unsaturated zone, notably on flow and transport modeling, subsurface heterogeneity, and parameter estimation. I will also briefly discuss the need for more effective communication between soil physicists globally, and stress the educational implications of a broader soil physics/soil science research perspective.

Water Flow and Solute Transport

Process-based descriptions of water and solute movement in the unsaturated zone are generally based on the classical Richards equation for variably-saturated water flow and the convection-dispersion equation for solute transport. These equations, summarized in Table 1, have been solved for a variety of one- and multi-dimensional applications. This paper focuses primarily on conceptual issues, and hence no attempt is made to provide an exhaustive review of available literature on vadose zone flow and transport modeling. Recent reviews of analytical and numerical modeling are given by Güven et al. (1990) and Sudicky and Huyakorn (1991).

Models based on Eqs. (1) and (2) in Table 1 have provided, and will continue to provide, indispensable tools in research and management. For example, they may be used for designing or analyzing specific experiments on water and solute movement; for extrapolating information gained from a limited number of field studies to different soil, crop, and climatic conditions, as well as to different tillage and water management schemes; for evaluating the comparative effects of alternative soil and water management practices and chemical application technologies on crop production and groundwater pollution; for remediation purposes; and for risk assessment studies involving specific pollution cases. The importance of model development and use should not be underestimated: models provide a means for organizing and integrating knowledge, give guidance to an experimental research program, while also being helpful for many practical management applications.

While models based on Eqs. (1) and (2) are important tools, they are also subject to a large number of simplifying assumptions which limit their applicability to many problems in the field. It my be instructive to list some of these limitations and assumptions. For example, the equations assume that (a) the air phase plays a relatively minor role during unsaturated flow, and hence that a single equation can be used to describe the variably-saturated flow process, (b) Darcy's equation is valid at both very low and very high flow velocities (including those occurring in structured soils), (c) the osmotic and electro-chemical gradients in the soil water potential are negligible, (d) the fluid density is independent of the solute concentration, and (e) matrix and fluid compressibilities are relatively small. The equations are further complicated

Table 1. Governing equations for one-dimensional variably-saturated water flow (Eq. 1) and convective-dispersive solute transport (Eq. 2).

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}[K(h)\frac{\partial h}{\partial z} - K(h)] + S \qquad (1)$$

$$\frac{\partial(\rho s)}{\partial t} + \frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial z}(\theta D\frac{\partial c}{\partial z} - qc) + \phi \qquad (2)$$

where C is the soil water capacity, i.e., the slope of the soil water retention curve, $\theta(h)$; θ is the volumetric water content, h is the soil water pressure head (negative for unsaturated conditions), t is time, z is distance from the soil surface downward, K is the hydraulic conductivity as a function of h or θ, s is the solute concentration associated with the solid phase of the soil, c is the solute concentration of the fluid phase, ρ is the soil bulk density, D is the solute dispersion coefficient, S and ϕ are sources and sinks for water and solutes, and q is the volumetric fluid flux (Darcy's law):

$$q = -K(h)\frac{\partial h}{\partial z} + K(h) \qquad (3)$$

For conditions of steady-state water flow in homogeneous soils, neglecting the source/sink term S and ϕ, and assuming linear sorption such that the adsorbed concentration (s) is linearly related to the solution concentration (c) through a distribution coefficient, k (i.e., $s=kc$), Eq (2) reduces to the standard convection-dispersion equation (CDE):

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} \qquad (4)$$

where $v = q/\theta$ is the averagepore water velocity, and $R = 1 + \rho k/\theta$ is the solute retardation factor.

---

by (f) the hysteretic nature of the retention function, $\theta(h)$, (g) the extreme nonlinearity of the hydraulic conductivity-function, K(k), (h) the lack of accurate and cheap methods for measuring the unsaturated hydraulic properties, (i) the extreme heterogeneity of the subsurface environment, and (j) inconsistencies between the scale at which the hydraulic and solute transport parameters in Eqs. (1) and (2) are usually measured, and the scale at which the predictive models are being applied. In addition, Eqs. (1) and (2) are formulated for isothermal soil conditions. In reality, most physical, chemical and microbial processes in the soil are strongly influenced by soil temperature. This also applies to water flow itself, including the indirect effects of temperature on the unsaturated soil hydraulic properties. Hence, a complete description of unsaturated zone transfer processes requires also consideration of heat flow and its nonlinear effect on most processes taking place in the soil-plant system.

Other limitations in the use of Eqs. (1) and (2) involve the source/sink terms S and ϕ in the flow and transport equations. The term S accounts primarily for water uptake by plant roots. While widely different approaches exist for simulating water uptake (e.g., Molz, 1981), most models currently used for water uptake are essentially empirical and contain parameters that depend on specific crop, soil, and environmental conditions. Much research is still needed to derive process-based descriptions of root growth and root water uptake as a function of water, salinity, temperature, and other stresses in the root zone, and to couple these descriptions with suitable crop growth models. Similarly, the source/sink term ϕ in Eq. (2) accounts for nutrient uptake and/or a variety of chemical and biological reactions and transformations insofar as these processes are not already included in the sorption/exchange term $\partial \rho s/\partial t$. These processes can be highly dynamic and nonlinear in time and space, especially for nitrogen and pesticide products. For example, among the nitrogen transformation processes that may need to be considered are nitrification, denitrification, mineralization, and nitrogen uptake by plants (Stevenson, 1982). For microbially induced organic and inorganic transformations, the degradation process should also consider the growth and maintenance of soil microbes.

Several simplifying assumptions are often also invoked when defining the sorption/exchange term $\partial \rho s/\partial t$ in Eq. (2). For example, the use of a constant retardation factor R in Eq. (4) assumes that a linear equilibrium isotherm can be used to describe solute interactions between the liquid and solid phases of the soil. While the use of a linear isotherm can greatly simplify the mathematics of a transport problem, sorption and exchange reactions are generally nonlinear and usually depend also on the presence of competing species in the soil solution. This, in turn, may require the coupling of Eq. 2) with suitable solution chemistry and/or ion exchange models (Mangold and Tsang, 1991; Šimunek and Suarez, 1994). The equilibrium assumption itself for sorption or exchange is often also questionable. A number of chemical-kinetic and diffusion-controlled "physical" models have been used to describe nonequilibrium transport. Attempts to model nonequilibrium transport have usually involved relatively simple first-order (one-site) kinetic rate equations. More refined nonequilibrium models have invoked the assumptions of two-site or multi-site sorption, and/or two-region (dual-porosity) transport involving solute exchange between mobile and immobile liquid transport (e.g., Wagenet, 1983; Brusseau et al., 1992). Models of this type have resulted in-better descriptions of observed laboratory and field transport data, in part by providing additional degrees of freedom for fitting observed concentration distributions. It should be noted that similar problems related to nonlinear and nonequilibrium'sorption also pertain to the transport of organic solutes (MacKay et al., 1985; Pinder and Abriola, 1986). Depending upon the type of chemical involved, models to predict organic transport in the unsaturated zone may also need to account for volatilization, microbial, chemical and photochemical transformations, and often multiphase flow with partitioning between different fluid phases (McCarty et al., 1984; Widdowson et al., 1988; Kaluarachchi and Parker, 1989).

The above limitations and assumptions regarding Eqs. (1) through (4) in Table 1 provide many opportunities for research. Unfortunately, there is ample evidence to suggest that solutions of these classical models, no matter how refined to include the most relevant chemical and microbiological processes and soil properties, fail to accurately describe transfer processes in most natural field soils. The one major factor responsible for this failure is the overwhelming heterogeneity of the subsurface environment. Heterogeneity occurs at a hierarchy of spatial and time scales (Wheatcraft and Cushman, 1991), ranging from microscopic scales involving time-dependent chemical sorption and precipitation/dissolution reactions, to intermediate scales involving the preferential movement of water and chemicals through macropores or fractures, and to much large scales involving the spatial variability of soils across the landscape. Several lines of research are being followed to deal with the different types of soil heterogeneity. On the one hand, subsurface heterogeneity can be addressed in terms of process-based descriptions which attempt to consider the effects of heterogeneity at one or several scales (kinetic sorption, preferential flow, field-scale spatial variability). On the other hand, subsurface heterogeneity is often also addressed using stochastic approaches which incorporate certain assumptions about the transport process in the heterogeneous system. Much can be learned from both approaches.

Preferential flow in structured media will be discussed below as an example of a process-based approach, followed by a brief overview of stochastic approaches.

Preferential Flow in Structured Media

Most soils contain macropores or other structural features associated with interaggregate pores, earthworm and gopher holes, decayed root channels, or drying cracks in fine-textured soils. Water and dissolved chemicals can move into and through such structured media with widely different velocities, thereby creating highly non-uniform flow fields. This process, often referred to as preferential flow, macropore flow, or short-circuiting, has been shown to occur not only in aggregated field soils (Beven and Germann, 1982; Gish and Shirmohammadi, 1991) and unsaturated fractured rock (Wang, 1991), but also in seemingly homogeneous soils because of fingering or some other unstable flow process (Hillel, 1993). While preferential flow can significantly affect infiltration rates at the soil surface, and unsaturated water flow in general, its main implications are likely the accelerated movement of surface-applied fertilizers, pesticides or other pollutants into and through the unsaturated zone.

Transport processes in structured media are often described using dual-porosity, two-region, or bi-continuum models. Models of this type assume that the medium consists of two interacting pore regions, one associated with the macropore or fracture network, and one with the micropores inside soil aggregates or rock matrix blocks. Different formulations arise depending upon how water and solute movement in the micropore region are modeled, and how the micropore and macropore regions are coupled.

Geometry-Based Models. A rigorous analysis of transport in structured soils can be made when the medium is assumed to contain geometrically well-defined cylindrical, rectangular or other types of macropores or fractures. Models may be formulated by assuming that the chemical is transported by convection, and possibly by diffusion and dispersion, through the macropores, while diffusion-type equations are used to describe the transfer of solutes from the larger pores into the micropores of the soil matrix. Table 2 illustrates such a model for transport through a soil system containing a series of parallel rectangular fractures. Similar models may be formulated for other aggregate geometries. Geometry-based transport models like those in Table 2 have been successfully applied to laboratory-scale experiments as well as to selected field studies involving mostly saturated conditions. As an example, Figure 1 shows calculated and observed Cl effluent curves from a 76-cm long undisturbed column of fractured clayey till. The extremely skewed (nonsigmoidal) shape of the effluent curve is a direct result of water and dissolved chemical moving mostly through the fractures and bypassing the soil matrix.

While geometry-based models are conceptually attractive, they may be too complicated for routine applications since structured field soils usually contain a mixture of aggregates of various sizes and shapes. More importantly, the problem of macropore and fluid flow continuity is not easily addressed with geometry-based flow models. The main objective of preferential flow studies should not be to quantify the macropore or fracture network per se, but rather the fluid flow network contained in some fashion within the fracture network. The issue of fluid flow continuity is critical, in part also since the macropore domain itself may be subject to preferential flow and channeling during unsaturated conditions. Finally, it is to be expected that the preferential flow paths will change with the degree of saturation during unsaturated flow. Some of these features are more easily considered using first-order models as discussed below.

Table 2. Governing equations for transport through soil containing parallel rectangular voids.

$$\vartheta_f R_f \frac{\partial c_f}{\partial t} + \vartheta_m R_m \frac{\partial c_m}{\partial t} = \vartheta_f D_f \frac{\partial^2 c_f}{\partial z^2} - \vartheta_f v_f \frac{\partial c_f}{\partial z} \tag{5}$$

$$R_m \frac{\partial c_a}{\partial t} = D_a \frac{\partial^2 c_a}{\partial x^2} \qquad (-a \leq x \leq a) \tag{6}$$

$$c_m(z,t) = \frac{1}{a} \int_0^a c_a(z,x,t)\,dx \tag{7}$$

where. the subscriptsfand m refer to the interaggregate (fracture f) and intra-aggregate (matrix m) pore regions, respectively, $c_a(z,x,t)$ is the local concentration in the aggregate, x is the horizontal coordinate, and D_a is the effective soil or rock matrix diffusion coefficient. Equation (5) describes vertical convective-dispersive transport through the fractures, while (6) accounts for linear diffusion in slab of width 2a in the horizontal (x) direction. Equation (7) represents the average concentration of the immobile soil matrix liquid phase Equations (5) and (6) are coupled using the assumption of concentration continuity across the fracture/matrix interface:

$$c_a(z,a,t) = c_f(z,t) \tag{8}$$

The water contents ϑ_f and ϑ_m in (6) are given in terms of the bulk soil volume, i.e.,

$$\vartheta_f = w_f \theta_f \qquad \vartheta_m = (1 - w_f)\theta_m \tag{9}$$

where w_f is the volume of the fracture pore system relative to that of the total soil pore system.

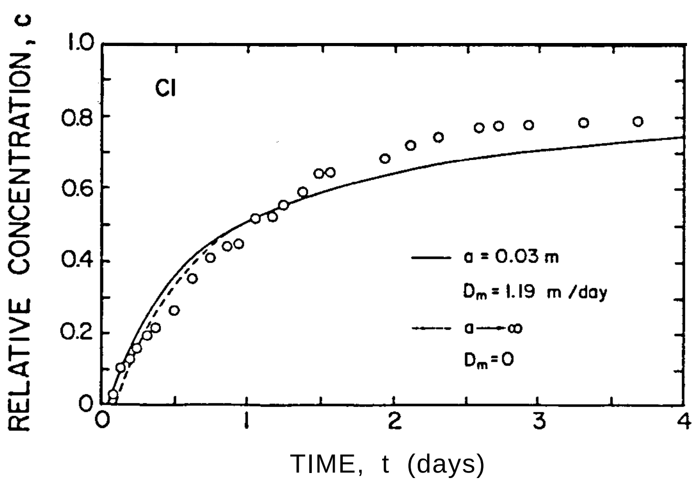

Fig. 1. Measured breakthrough curve for Cl transport through fractured clayey till (open circles; data from Grisak et al., 1980). The solid line was obtained with the exact solution (e.g., van Genuchten, 1985) of the model in Table 2 using parameter values given by Grisak et al. (1980). The dashed line was obtained by ignoring dispersion in the interaggregate region (D_f=0) and allowing the fracture spacing to go to infinity ($a \rightarrow \infty$).

Table 3. Governing equations for transport in structured media assuming first-order solute exchange between mobile and immobile liquid regions:

$$\vartheta_f R_f \frac{\partial c_f}{\partial t} + \vartheta_m R_m \frac{\partial c_m}{\partial t} = \vartheta_f D_f \frac{\partial^2 c_f}{\partial z^2} - \vartheta_f v_f \frac{\partial c_f}{\partial z} \tag{10a}$$

$$\vartheta_m R_m \frac{\partial c_m}{\partial t} = \alpha(c_f - c_m) \tag{10b}$$

where a is a first-order solute mass transfer coefficient characterizing diffusional exchange of solutes between the mobile and immobile liquid phases. Notice that (10a) is identical to (5) for the rectangular geometry-based model. The mass transfer coefficient is of the general form

$$\alpha = \frac{\beta \vartheta_m D_a}{a^2} \qquad \alpha = \frac{\beta \vartheta_m D_a}{(\xi_o - 1)^2} \tag{11a,b}$$

where β is a geometry-dependent shape factor, and a is the characteristic length of the aggregate (e.g., the radius of a spherical or solid cylindrical aggregate, or half the width of a rectangular aggregate) Equation (1 lb) holds for a hollow cylindrical macropore for which $\xi_o = b/a$ where a now represents the radius of the macropore and b the outer radius of the cylindrical soil mantle surrounding the macropore. The value of β ranges from 3 for rectangular **slabs to 15 for** spherical aggregates [van Genuchten and Dalton, 1990].

First-Order Models. Rather than using geometry-based transport models, many of the preferential flow features can also be accounted for using models which assume first-order exchange of solutes by diffusion between the macropore (mobile) and micropore (immobile) liquid regions. Table 3 summarizes the governing equations for such an approach, Models of this type have been popularly used in petroleum and chemical engineering studies; they lump the effects of aggregate size, geometry, and the diffusion coefficient in the quasi-empirical mass transfer coefficient, α. Because of their simplicity, first-order mobile-immobile models can be included in one- and multi-dimensional numerical models with only minimal changes in the computer codes. The applicability of first-order rate models to transport processes at the scale of laboratory soil columns has been demonstrated in a large number of studies in the soil physics literature (Nielsen et al., 1986; van Genuchten et al., 1990).

Extension to Variably-Saturated Flow. One limitation of mobile-immobile transport models such as those described in Tables 2 and 3 is the assumption that water flow is limited to the macropore region. This assumption is inconsistent with experimental observations which indicate that water in the soil matrix is generally also mobile. Different types of models have been proposed to simulate transport in variably-saturated structured media. As an example, Table 4 summarizes the dual-porosity model developed by Gerke and van Genuchtcn (1993). This model assumes that the Richards equation for transient water flow and the convection-dispersion equation for solute transport can be applied to each of the two pore systems. Similarly as for the first-order mobile-immobile transport models, water and solute mass transfer between the two pore systems is described with first-order rate equations. The model in Table 4 contains two water retention functions, one for the matrix and one for the fracture pore system, but three hydraulic conductivities functions: $K_f(h_f)$ for the fracture network $K_m(h_m)$

for the matrix, and K,(h) for the fracture/matrix interface. The $K_f(h_f)$ function is determined by the structure of the fracture pore system, i.e., the size, geometry, continuity and wall roughness of the fractures, and possibly the presence of fracture fillings. Similarly, $K_m(h_m)$ is determined by the hydraulic properties of single matrix blocks, and the degree of hydraulic contact between adjoining matrix blocks during unsaturated flow. Finally, $K_a(h)$ is the effective hydraulic conductivity function to be used in Eq. (14) for describing the exchange of water between the two pore systems.

Table 4. Governing equations for variably-saturated flow and solute transport in a dual-porosity medium [Gerke *and van* **Genuchten,** 1993]

Flow equations for the fracture (subscript f) and matrix (subscript m) pore ***systems are,*** respectively,

$$C_f \frac{\partial h_f}{\partial t} = \frac{\partial}{\partial z}\left(K_f \frac{\partial h_f}{\partial z} - K_f\right) - \frac{\Gamma_w}{w_f} \tag{l2a}$$

$$C_m \frac{\partial h_m}{\partial t} = \frac{\partial}{\partial z}\left(K_m \frac{\partial h_m}{\partial z} - K_m\right) + \frac{\Gamma_w}{1 - w_f} \tag{12b}$$

where Γ_w describes the rate of exchange of water between the fracture and matrix regions:

$$\Gamma_w = \alpha_w (h_f - h_m) \tag{13}$$

in which α_w is a first-order mass transfer coefficient for water:

$$\alpha_w = \frac{\beta}{a^2} K_a \gamma_w \tag{14}$$

where β and a are as defined in Table 3, K_a is the hydraulic conductivity of the fracture/matrix interface, and $\gamma_w\,(=0.4)$ is a dimensionless scaling factor. Solute transport for the fractures and matrix are given by, respectively:

$$\frac{\partial}{\partial t}(\theta_f R_f c_f) = \frac{\partial}{\partial z}\left(\theta_f D_f \frac{\partial c_f}{\partial z} - q_f c_f\right) - \frac{\Gamma_s}{w_f} \tag{15a}$$

$$\frac{\partial}{\partial t}(\theta_m R_m c_m) = \frac{\partial}{\partial z}\left(\theta_m D_m \frac{\partial c_m}{\partial z} - q_m c_m\right) + \frac{\Gamma_s}{1 - w_f} \tag{15b}$$

where Γ_s is the solute mass transfer term given by

$$\Gamma_s = \alpha(c_f - c_m) + \begin{cases} \Gamma_w \vartheta_f c_f/\theta & \Gamma_w \geq 0 \\ \Gamma_w \vartheta_m c_m/\theta & \Gamma_w < 0 \end{cases} \tag{16}$$

in which α is the same as used in the first-order mobile-immobile model (Table 3). The first term on the right-hand side of (16) specifies the diffusion contribution to Γ_s, while the second term gives the convective contribution. The above variably-saturated dual-porosity transport model reduces to the first-order model (Table 3) for conditions of steady-state flow in the fracture (macropore) region and no flow in the matrix pore system ($q_m = \Gamma_w = 0$).

Several important features of preferential flow are illustrated here by using the model in Table 4 to calculate the infiltration of water at a constant rate of 50 cm/day into a 40-cm deep structured soil profile having an initially uniform pressure head of -1000 cm. Water is allowed to infiltrate exclusively into the fracture pore system, thus assuming that the matrix pore system at the soil surface is sealed. The hydraulic properties of the fracture and matrix pore systems (Fig. 2) are indicative of relatively coarse- and fine-textured soils, respectively. The simulations assume a macroporosity of 5% (w_f=0.05), and rectangular aggregates (β=3) having a width of 2 cm (a = 1 cm). The hydraulic parameters for $K_a(h)$ were assumed to be the same as those for $K_m(h_m)$, except for the saturated hydraulic conductivity which was decreased by a factor of 100. Figure 3 shows simulated pressure head and watercontent distributions during infiltration. The results indicate a rapid increase in the pressure head of the fracture pore system, but a relatively slow response of the matrix (Fig. 3a). The resulting pressure head gradient between the two pore systems causes water to flow from the fracture into the matrix pore system (Fig. 3b), thus increasing the water content of the matrix (Fig. 3c). Significant pressure head differences between the two pore systems are still present when the infiltration front in the fracture system reaches the bottom of the soil profile after approximately 0.08 days (Fig. 3a). Notice that the water transfer rate, I’,,,, is highest close to the infiltration front, and gradually decreases toward the soil surface (Fig. 3b). The shapes of the Γ_w-curves reflect the combined effects on I’, of the pressure head difference between the two pore regions (which decreases in time) and the value of K_a (which increases in time) at any point behind the wetting front.

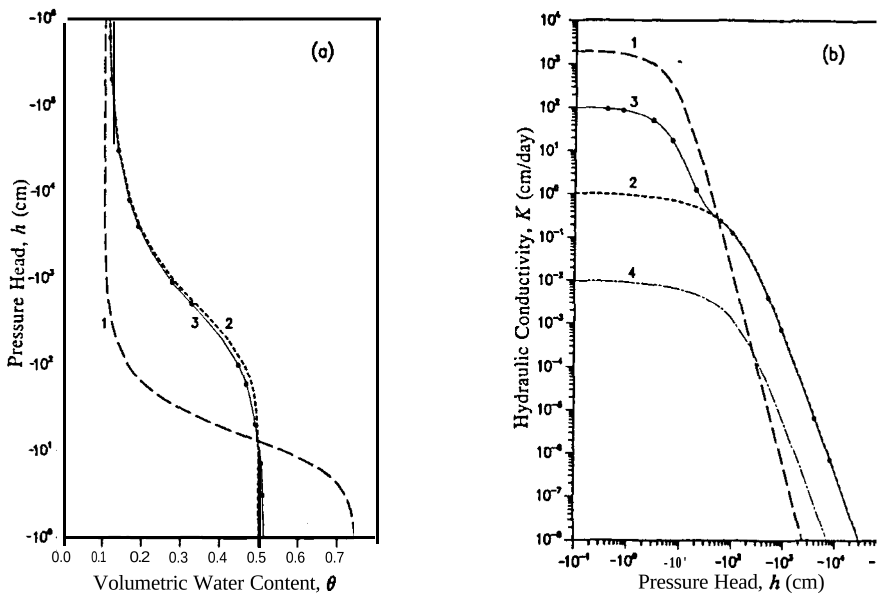

Fig. 2. Water retention (a) and hydraulic conductivity (b) functions of a dual-porosity medium involving the fracture network (l), the matrix pore system (2), the composite medium (3), and the conductivity of the fracture/matrix interface (4) (after Gerke and van Genuchten, 1993).

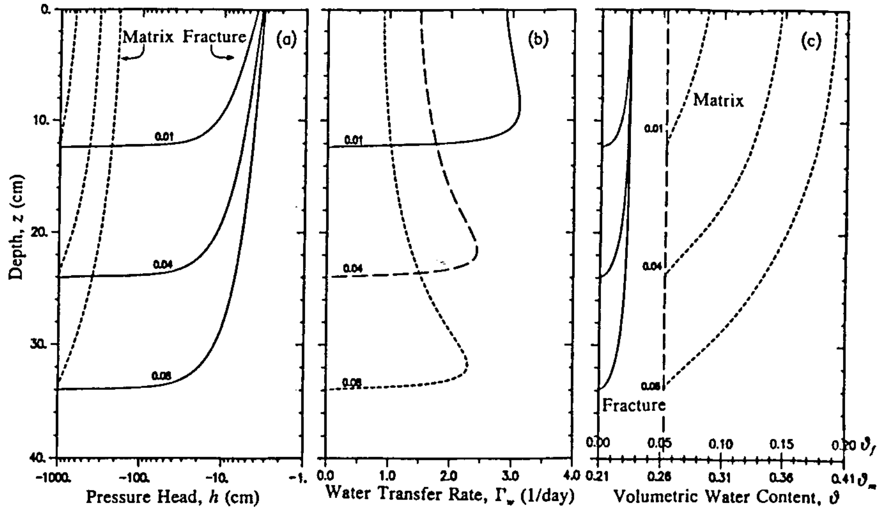

Fig. 3. Simulated distributions versus depth of (a) the pressure head, h, (b) the water transfer rate, Γ_w, and (c) the volumetric water content, ϑ, for the matrix (dashed lines) and fracture (solid lines) pore systems at t=0.01, 0.04, and 0.08 days (after Gerke and van Genuchten, 1993).

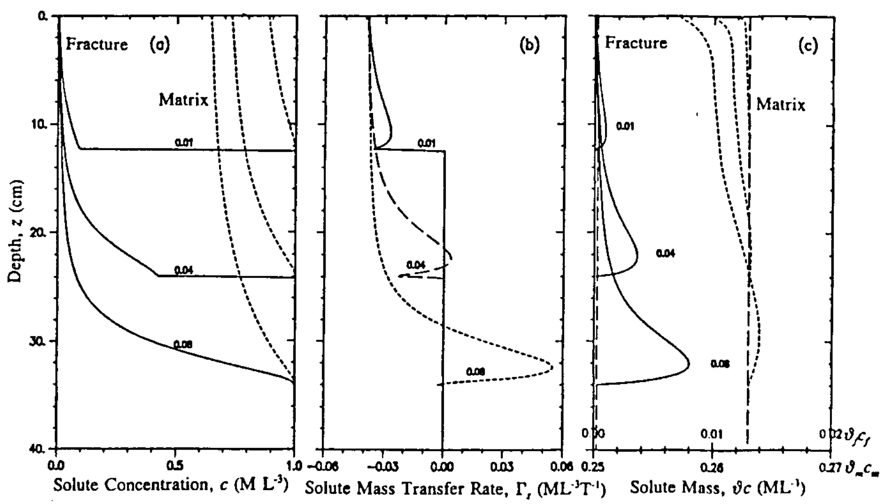

Fig. 4. Simulated distributions versus depth of (a) the solute concentration, c, (b) the solute transfer rates, Γ_s, and (c) the solute mass, ϑc, for the matrix (dashed lines) and fracture (solid lines) pore systems at t=0.01, 0.04, and 0.08 days (after Gerke and van Genuchten, 1993).

Figure 4 shows the simulated concentration distributions. Results are for the infiltration of solute-free water into a structured medium having a relative initial concentration of 1. The calculations show that the solute concentrations in the fracture pore system initially decrease rapidly as solute-free water infiltrates (Fig. 4a). Water with relatively low solute concentration subsequently flows from the fracture into the matrix pore system (see also Figure 3b). At the same time, however, solutes begin to diffuse back from the matrix into the fracture pore system because of the large concentration gradients which develop between the two pore systems (Fig. 4a). The net solute transfer rate, Γ_s, eventually becomes negative, indicating a net transfer from the matrix into the fracture pore system (Fig. 4b). The solute mass in the matrix pore system ($\vartheta_m c_m$) initially decreases only slightly (t=0.01 days in Figure 4c), but starts to decrease more rapidly at later times ($t \geq 0.04$ days). The results in Figure 4 illustrate the extremely transient and complicated nature of transport in a structured medium involving vertical convective transport and dispersion; and horizontal mass transfer by convection and diffusion. Simulations such as those shown in Figures 3 and 4 may be used to explain previously observed effects of several parameters on solute leaching during transient flow, including soil surface boundary condition (Bond and Wierenga, 1990) water application rate (White et al., 1986; McLay et al., 1991), and initial condition (Kluitenberg and Horton, 1990).

The potential value of process-based preferential flow simulations is further illustrated in Figure 5 which shows the sensitivity of the infiltration process to changes in the hydraulic conductivity K_a of the fracture/matrix interface. Results obtained with a relatively large saturated conductivity, $K_{s,a}$, of 1 cm/day (equal to the matrix conductivity) closely approximate the limiting case of pressure head equilibrium (Fig. 5a) with little or no preferential flow. The equilibrium moisture front reaches a depth of only 5 cm after 0.02 days. The water transfer rates shown in Figure 5b are So high that the two pore systems quickly approach equilibrium when $K_{s,a} = 1$ cm/day. However, for the smallest $K_{s,a}$ (0.001 cm/day) water percolated rapidly downward through the fracture pore system to a depth of 35 cm during the same time period (t=0.02 days or 29 minutes). This last situation represents an extreme case of preferential flow with significant pressure head differences between the two pore systems (Fig. 5a).

The results in Figure 5 are important since they indicate that equilibrium between the fracture and matrix pore systems should be expected when the hydraulic conductivity, $K_{s,a}$, of the matrix/fracture interface is equal to the conductivity of the soil matrix (assuming a fracture spacing of 2 cm). For preferential flow to initiate, $K_{s,a}$ must be much less than $K_{s,m}$ of the matrix. This conclusion is consistent with experimental studies which suggest that a soil aggregate may have a higher local bulk density (and hence lower conductivity) near its surface than in the aggregate center, presumably because of the deposition of organic matter, fine-texture mineral particles, or various oxides and hydroxides on the aggregate exteriors or macropore walls. For example, Wilding and Hallmark (1984) noted that ped argillans have been demonstrated to markedly reduce rates of diffusion and mass flow from the ped surface to the soil matrix. Cutans, consisting of coatings with modified physical, chemical or biological properties, may have preferred orientations parallel to the aggregate surfaces; they are common in many clayey horizons as a consequence of both natural and tillage-induced deformation. Unsaturated fractured rock formations may exhibit similar features, i.e., fracture skins (Moench, 1984) or other types of coatings (Wang and Narasimhan, 1985; Pruess and Wang, 1987; Thoma et al., 1992) made up of fine clay particles, calcite, zeolites, or silicates, which may reduce the hydraulic conductivity. Preferential flow within the macropores or fractures themselves also

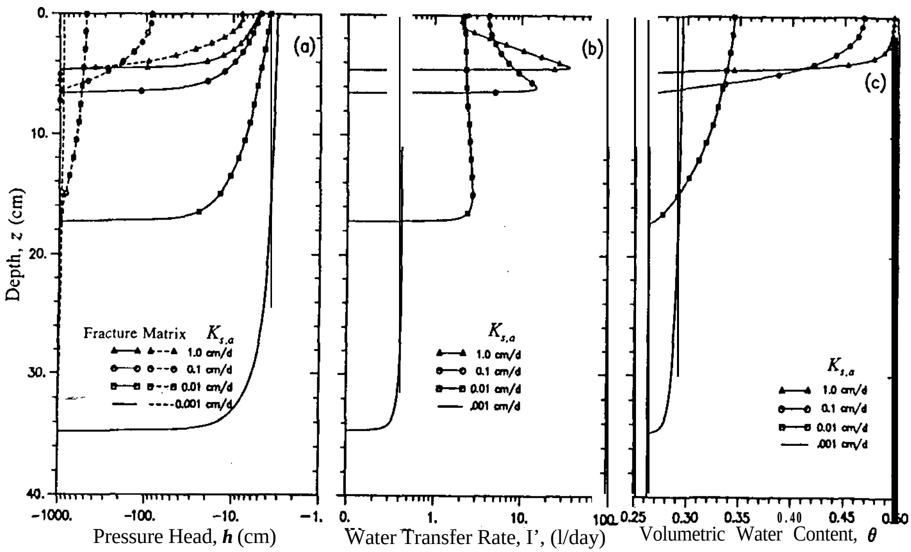

Fig. 5. Simulated distributions versus depth of (a) the pressure head, h, (b) the water transfer rate, Γ_w, and (c) the total volumetric water content, θ, for different values of the interface hydraulic conductivity, $K_{s,a}$ ($t = 0.02$ days, a = 1 cm).

contributes to a lower effective $K_a(h)$. Such a situation would restrict water and solute exchange between the two pore systems (notably infiltration into the matrix) to only a small portion of the total interface area (Hoogmoed and Bouma, 1980), even in capillary-size pores (Omoti and Wild, 1979). Hydrophobic fracture surfaces can similarly restrict the exchange between the two pore systems.

Application of the model in Table 4 requires several hydraulic and other parameters which are not easily measured. Estimates for the K_f- and K_m -functions (Fig. 2) may be obtained by assuming that K_f is primarily the conductivity function in the wet range, while K_m is the conductivity in the dry range (Othmer et al., 1991; Durner, 1992; Peters and Klavettcr, I988). Obtaining accurate estimates for the hydraulic properties of the fracture **pore** system from the composite curves requires that the hydraulic functions be very well defined in the wet range. This problem is indirectly demonstrated by Figure 2a which was obtained by assuming that the fracture pore system comprises 5% of the porous medium. Notice that the retention function of the matrix differs only minimally from that of the composite medium. Hence, it may be very difficult in practice to estimate separate soil water retention curves of the fracture and matrix pore systems using bulk soil measurements which generally contain some noise. By contrast, it appears more promising to assess the contributions of macropores from an accurately measured bulk hydraulic conductivity function near saturation (e.g., Smettem and Kirby. 1990).

Finally, we note that the dual-porosity model in Table 4 assumes applicability of the Richards equation, and hence of Darcy's law. This assumption may not be strictly correct for the fracture pore system. However, given the uncertainties in all of the physical and chemical processes related to preferential flow, the real issue is not necessarily the validity of Darcy's law as such, but whether Darcy's law - even if formally invalid - can provide a useful description of the preferential flow process. Alternative descriptions of the flow regime in fractures, such as Manning's equation for turbulent overland flow, kinematic wave theory, or simple gravity-flow models, may be too elaborate for routine use. Moreover, some of these approaches do not have provisions for flow to occur from the micropores back into the fractures, e.g., at or near the bottom boundary of a coarse-textured soil horizon overlaying a fine-textured horizon.

Stochastic Approaches

Dual-porosity type preferential flow models represent attempts to deal with pore structure heterogeneity at spatial scales somewhere intermediate between laboratory-scale measurements and the larger field scale. As such they are useful for predicting predominantly vertical transport in structured but areally homogeneous field soils. Unfortunately, few soils are areally homogeneous. This is illustrated in Figure 6 which shows measured bromide concentrations some 400 days after application of an areally uniform instantaneous bromide pulse to the surface of a field soil in Switzerland. The unequal distribution of the tracer, especially horizontally along the transect, raises important questions about how to design effective field sampling programs, which field instrumental methods to use for sampling, and how to simulate the heterogeneous field-scale transport process.

The enormous variability of the subsurface environment, and the imprecision with which parameters and processes can be measured, has led to the adoption of stochastic models and geostatistical procedures to assist in the prediction and monitoring of contaminant transport in

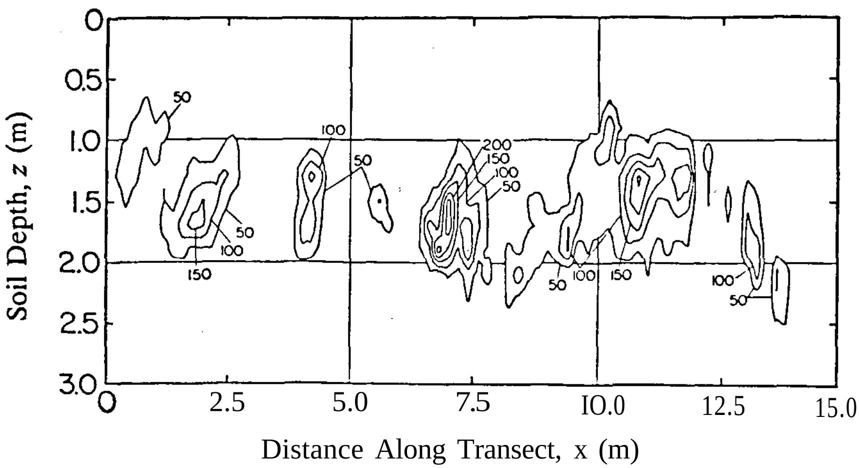

Fig. 6. Observed gravimetric bromide concentrations (mg per kg dry soil) 399 days after application of a bromide tracer pulse to the soil surface (after Schulin et al., 1987).

the unsaturated zone. A large number of stochastic approaches are currently available (Dagan, 1989; Jury and Roth, 1990), including scaling theories, Monte Carlo methods, and stochastic-continuum models. A common assumption of most stochastic transport models is that parameters are treated as random variables with values assigned according to a given probability distribution. In practice, the stochastic approach is often used with several simplifying assumptions, including (1) the stationarity hypothesis which assumes that a random parameter has the same probability density function (pdf) at every point in the field, and (2) the ergodicity hypothesis which states that ensemble averages can be replaced by spatial averages, and that spatial replicates can be used to construct the appropriate pdfs for the transport parameters.

Current scaling theories applied to field-scale flow and transport problems have evolved from the early work of Miller and Miller (1956) on microscopic geometric similitude. The approach considers different regions of a heterogeneous field soil to be similar if their microscopic geometric structures are scale magnifications of each other. Transport parameters at any point within a given field soil are related to the parameters at an arbitrary reference point through length scale ratios, or scaling factors. Hydraulic conductivity and soil water retention parameters at a particular location in the field are then calculated from those of the reference soil by means of prescribed equations (Nielsen et al., 1983; Sposito and Jury, 1985). Recent work (Jury et al., 1987; Vogel et al., 1991) suggests that two or more scaling factors may be needed for soils which are not strictly similar. Most previous applications of scaling theory to field problems assumed that the scaling factor is a random variable characterized by a certain probability density function. The method has been a central part of the stochastic flow and transport models of Bresler and Dagan (1983) and Dagan and Bresler (1983).

Monte Carlo simulations assume that the flow and transport parameters are random variables with values assigned from a joint pdf. The water flow or solute transport equations are repeatedly solved using coefficient values from the assumed pdf until a large number of possible outcomes has been generated. These outcomes are then used to calculate sample means and variances of the underlying stochastic transfer process. The method may be used to demonstrate, among other things, that macrodispersion in field soils is affected primarily by pore-water velocity variations, and much less by local dispersion phenomena (Amoozegard-Fard et al. 1982; Persaud et al., 1985).

Stochastic continuum models were initially used primarily in groundwater studies (e.g., Gelhar et al., 1979; Gelhar and Axness, 1983). In these models all random variables are represented by the sum of their mean values plus random fluctuations which, when substituted into the convection-dispersion equation (Eq. 4) lead to a new mean transport model with additional terms. The modified model may be evaluated by deriving first-order approximations for the fluctuations and solved by means of Fourier transforms. The approach leads to, among other things, a macro-scale dispersion coefficient whose value is reached asymptotically as distance and/or time increase. Spatial correlations of solute velocity variations characterized by its autocorrelation function, have been shown to play important roles in the derivation of the asymptotic convection-dispersion equation (Sposito et al., 1986).

A different continuum approach was followed by Simmons (1982) who neglected the dispersion coefficient D in Eq. (4), and developed a formal theoretical approach using the pore-water velocity and the travel time as random variables. Jury (1982) initially also neglected D in his development of the transfer function model (TFM) of solute transport. The TFM involves the use of a probability density function, $f_L(t)$, of travel times from the soil surface down to some reference depth L. The travel time probability density function for many transport experiments is given by a lognormal distribution. The flux concentration in the profile is represented with a convolution integral of $f_L(t)$ and the imposed flux concentration at the soil surface. Transfer function models are expected to find increasingly wider applications in subsurface solute transport as the underlying theory is being strengthened by the incorporation of a variety of physical, chemical and biological processes (Jury and Roth, 1990; Sardin et al., 1991).

Several other statistical approaches exist, including the use of continuous Markov processes (e.g., Knighton and Wagenet, 1987), fractal-mathematics (Wheatcraft and Cushman, 1991), random walk methods (Kinzelbach, 1988), and a variety of procedures based on moment analysis (Cvetkovic, 1991). More work in these areas of research can be expected in the near future. While useful, the real challenge is to eventually include in the stochastic approach those physical, chemical and microbiological processes and soil properties known to affect macroscopic transport behavior. In other words, the challenge is to combine stochastic behavior with process-based knowledge that so painstakingly has been obtained over the past several hundred or more years. It would be a major error to ignore this knowledge and to resort to a purely empirical-statistical description of field-scale transport processes. Moreover, several farming practices or edaphic factors sometimes combine to produce an apparent stochastic situation which, upon closer inspection, may be described or interpreted more advantageously in terms of deterministic processes or soil properties. An excellent example is given by Rhoades (1994) on field-scale variations in soil salinity measured with standard methods as well as using an automated, tractor-driven measurement system.

Parameter Estimation

The past several decades has seen a tremendous increase in the development and use of computer models simulating various aspects of water and solute movement in the unsaturated zone. The rapid proliferation of computer models in research and management will likely continue as computer costs keep decreasing and the need for more realistic predictions increases. Unfortunately, the simulation of field-scale processes requires considerable effort in quantifying a large number of spatially and temporally variable soil hydraulic and solute transport parameters. It is likely that the completeness of experimental data, and the accuracy of the estimated model parameters, eventually will become critical factors determining the usefulness of site-specific simulations. Many of our current methods for measuring relevant unsaturated flow and transport parameters are largely those that were introduced several decades ago (Klute, 1986; Dane and Molz, 1991). New methods and technologies of measurement are critically needed to keep pace with our ability to simulate increasingly complex laboratory and field systems. New or improved instrumental methods must be developed to more accurately and cost-effectively measure pertinent physical and chemical soil properties, including especially the unsaturated hydraulic functions. At the same time, given suitable instrumentation, challenges are to improve current methods for sampling design and optimal analysis of laboratory and field experiments.

Instrumental Techniques. A number of potentially very powerful geophysical and related approaches are now available for rapid non-invasive as well as in-situ measurements within the unsaturated zone. Among the non-invasive methods are (a) electromagnetic methods (EM) for characterizing soil salinity and water content, (b) ground penetrating radar (GPR) methods for detecting subsoil layers (e.g., those causing preferential flow), (c) nuclear magnetic resonance (NMR) techniques for studying soil porosity and permeability, and (d) X-ray computed tomography (CT) for studying, among other things, the three-dimensional geometry and continuity of macropores. Similarly, time-domain reflectometry (TDR) methods are increasingly being used for in-situ measurements of water content and/or salinity distributions, both in the laboratory as well as in the field. The same is true for remote sensing techniques to obtain spatial and temporal distributions of soil moisture. More sophisticated equipment for measuring the soil hydraulic conductivity is also becoming available, including a variety of new or improved borehole and disk permeameters.

Inverse Methods. Inverse procedures provide potentially powerful methodologies to more accurately estimate a large number of water flow, solute transport, and other parameters. Early studies using inverse procedures focused primarily on solute transport problems by coupling appropriate parameter optimization methods with analytical solutions of the convection-dispersion equations (e.g., van Genuchten, 1981). Starting with the studies of Zachmann et al. (1981) and Dane and Hruska (1983), the method was later extended to the analysis of unsaturated soil hydraulic functions. Computer models applicable to one-step and multi-step laboratory outflow measurements are given by Kool et al. (1985), van Dam et al., (1990) and Eching and Hopmans (1993). While initially applied primarily-to laboratory type experiments, inverse methods are equally well applicable to field data, or some appropriate combination of field and laboratory data. As such, inverse methods are extremely flexible and could involve nearly any combination of observed water flow data (water contents, pressure heads, fluxes), solute transport data (concentrations, fluxes), and heat transfer data (temperature, heat fluxes), to yield simultaneously estimated hydraulic parameters (hysteretic water retention and unsaturated conductivity parameters), solute transport parameters (pore-water velocities, retardation factors, dispersion coefficients, degradation coefficient, nonequilibrium rate coefficients), and/or heat transfer parameters (soil thermal conductivity, volumetric heat capacity). Formally, there is also no reason to limit the analysis to only one- or two-dimensions.

Application of inverse methods to observed field data appears especially promising, e.g., procedures that estimate soil hydraulic parameters from infiltration experiments (Russo et al., 1991) rather than using the much more time-consuming gravity-drainage (instantaneous profile) approach (Shouse et al., 1992). Another advantage of inverse procedures, if formulated within the context of a parameter optimization problem, is that a detailed error analysis of the estimated parameter can be incorporated more easily into the procedure. lnverse procedures may prove to be very appropriate for estimating regional-scale effective soil hydraulic parameters, either by appropriately manipulating in-situ measurement of the hydraulic properties as shown by Feddes et al. (1993), or perhaps by using remotely-sensed measurements of the soil surface water content.

Concluding Remarks

This paper gives a brief overview of some of the issues facing soil physicists and others in accurately predicting, measuring, and managing water and chemical transport processes in the unsaturated zone. The rapidly increasing problems of soil and water pollution require an integrated, multi-disciplinary research effort involving contributions within the soil sciences from soil physicists, soil biologists, soil morphologists and soil geneticists, as well as expertise from outside soil science in hydrology, geology, micrometeorology, the atmospheric sciences, and especially mathematics and computer science. The implementation of a multidisciplinary approach is predicated first and foremost by a level of awareness that such an approach is needed in our own individual research effort, rather than necessarily being a member of a large mission-oriented multidisciplinary research group. As such, I do believe that the international soil science community needs to restructure some of its activities. For example, most members of the Soil Science Society of America (SSSA) and the International Soil Science Society (ISSS) operate and publish their research products within strongly disciplinary divisions or commissions, with a concomitant lack of interaction across disciplinary boundaries.

We also must do a better job in documenting our research products. A large number of models have been developed for predicting water and contaminant transport in the subsurface, as well as for geostatistically analyzing spatially variable soil properties. These models must be documented and made available more effectively to our peers, as well as to users in extension or the private sector. An international clearinghouse (van der Heijde, 1993) for computer models has been established for this purpose. A similar clearinghouse is sorely needed for databases on flow and transport experiments carried out by soil physicists and others. Designing and conducting field experiments on water flow and solute transport, especially in naturally heterogeneous field soils, can be extremely costly and time-consuming in terms of manpower, equipment, and analytical expenses. It is imperative that such experiments be properly documented and its results be made available to the scientific community at large. The same is true for the documentation of measured unsaturated soil hydraulic-data sets (van Genuchten and Leij, 1992). Some of these data sets are the results of thousands of hours of work. The International Soil Science Society could play an important leadership role in such efforts to document research results.

Finally, the need for a more broadly defined soil physics/soil science framework has many educational implications. We, as soil physicists, must become increasingly familiar with the principles of computer science, mathematics, fluid dynamics, hydrogeology, and micrometeorology, and perhaps also with such topics as radiation physics, ecosystems management, and global-scale hydrology. This training should not only occur at the level of graduate education, but also at the undergraduate level or even earlier (see also discussion in Sposito and Reginato, 1992).

Literature **Cited**

1. Amoozegard-Fard, A., D. R. Nielsen, and A. W. Warrick. 1982. Soil solute concentration distributions for spatially varying pore water velocities and apparent diffusion coefficients. Soil Sci. Soc. Am. J. 46(1):3-9.
2. Beven, K. J., and P. Germann. 1982. Macropores and water flow in soils. Water Resour. Res. 18:1311-1325.
3. Bond, W. J., and P. J. Wierenga. 1990. Immobile water during solute transport in unsaturated sand columns. Water Resour. Res. 26:2475-2481.
4. Bresler, E., and G. Dagan. 1983. Unsaturated flow in spatially variable fields. 3. Solute transport models and their application to two fields. Water Resour. Res. 19(2):429-435.
5. Brusseau, M. L., R. E. Jessup, and P. S. C. Rao. 1992. Modeling solute transport

influenced by multiprocess nonequilibrium and transformation reactions. Water Resour. Res. 28(1):175-182.

6. Cvetkovic, V. D. 1991. Mass arrival of reactive solute in single fractures. Water Resour. Res. 27(2):177-183.
7. Dagan, G. 1989. Flow and Transport in Porous Formations. Springer Verlag, Berlin.
8. Dagan, G., and E. Bresler. 1983. Unsaturated flow in spatially variable fields. 1. Derivation of models of infiltration and redistribution. Water Resour. Res. 19(2):413-420.
9. Dane, J. H., and S. Hruska. 1983. In-situ determination of soil hydraulic properties during drainage. Soil Sci. Soc. Am. J. 47:619-624.
10. Dane, J. H., and F. J. Molz. 1991. Physical measurements in subsurface hydrology. Rev. of Geophys., Vol. 29, Supplement, pp. 268-279.
11. Dumer, W. 1992. Predicting the unsaturated hydraulic conductivity using multi-porosity water retention functions. In: M. Th. van Genuchten, F. J. Leij and L. J. Lund (eds.), Proc. Int. Workshop on Indirect Methods for Estimating the Hydraulic Properties of Unsaturated Soils, pp. 185-202, Univ. of California, Riverside, CA.
12. Eching, S. O., and J. W. Hopmans. 1993. Inverse Solution of Unsaturated Soil Hydraulic Functions from Transient Outflow and Soil Water Pressure Data. Land, Air and Water Resources Paper No. 100021, Dept. of Land, Air and Water Resources, Univ. of California, Davis.
13. Evans, D. D., and T. J. Nicholson (eds.). 1987. Flow and Transport Through Unsaturated Fractured Rock. Am. Geophys. Union, Washington, D.C.
14. Feddes, R. A, G. H. de Rooij, J. C. van Dam, P. Kabat, P. Droogers, and J. N. M. Stricker. 1993. Estimation of regional effective soil hydraulic parameters by inverse modeling. In: D. Russo and G. Dagan (eds.), Water Flow and Solute Transport in Soils, pp. 211-230, Springer Verlag, New York, NY.
15. Gelhar, L. W., and C. L. Axness. 1983. Three-dimensional stochastic analysis of macrodispersion in aquifers. Water Resour. Res. 19(1):161-180.
16. Gelhar, L. W., A. L. Gutjahr, and R. N. Naff. 1979. Stochastic analysis of macro-dispersion in aquifers. Water Resour. Res. 15(6):1387-1397.
17. Gerke H. H., and M. Th. van Genuchten. 1993. A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. Water Resour. Res. 29(2):305-319.
18. Gish, T. J., and A. Shirmohammadi (eds.). 1991. Preferential Flow, Proc. of the National Symp. December 16-17, 1991, Chicago, Illinois. Am. Soc. Agric. Eng., St. Joseph, MI.
19. Grisak, G. E., J. F. Pickens, and J. A. Cherry. 1980. Solute transport through fractured media, 2. Column study of fractured till. Water Resour. Res. 16:731-739.
20. Giiven, O., F. J. Molz, and J. G. Melville. 1990. Modeling migration of contaminants in the subsurface environment. In: J. Saxena (ed.), Hazard Assessment of Chemicals, pp. 203-282, Hemisphere Publ. Co., New York, NY.
21. Hillel, D. 1990. Fundamentals of Soil Physics. Academic Press, New York, NY.
22. Hillel, D. 1993. Unstable flow: A potentially significant mechanism of water and solute transport to groundwater. In: D. Russo and G. Dagan (cds.), Water Flow and Solute Transport in Soils, pp. 123-135, Springer Verlag, New York, NY.
23. Hoogmoed, W. B., and J. Bouma. 1980. A simulation model for predicting infiltration into cracked clay soil. Soil Sci. Soc. Am. J. 44:458-461.
24. Jury, W. A. 1982. Simulation of solute transport using a transfer function model, Water Resour. Res. 18(2):363-368.

25. Jury, W. A., and K. Roth. 1990. Transfer Functions and Solute Movement in Soil; Theory and Applications. Birkhäuser Verlag, Basel.
26. Jury, W. A., D. Russo, and G. Sposito. 1987. Spatial variability of water and solute transport in unsaturated soil, II. Scaling models of water transport, Hilgardia. 55:33-55.
27. Kaluarachchi, J. J., and J. C. Parker. 1989. An efficient finite element method for modeling multiphase flow. Water Resour. Res. 25(1):43-54.
28. Kinzelbach, W. 1988. The random walk method in pollutant transport simulation. In: E. Custodio, A. Gurgui, and J. P. Lobo Ferreira (eds.), Groundwater Flow and Quality Modeling. pp. 227-246, D. Reidel, Hingham, MA.
29. Kluitenberg, G. J., and R. Horton. 1990. Effect of solute application method on preferential transport of solutes in soil. Geoderma, 46:283-297.
30. Klute, A. (ed.). 1986. Methods of Soil Analysis, part 1. Physical and Mineralogical Methods. Agronomy 9, 2nd ed., Am. Soc. Agron., Madison, WI.
31. Knighton, R. E., and R. J. Wagenet. 1987. Simulation of solute transport using a continuous time Markov process, I. Theory and steady-state application. Water Resour. Res. 23(10):1911-1916.
32. Kool, J. B., J. C. Parker, and M. Th. van Genuchten. 1985. ONESTEP: A nonlinear parameter estimation program for evaluating soil hydraulic properties from one-step outflow experiments. Virginia Agric. Exp. Stat. Bull. 85-3, Blacksburg, VA.
33. MacKay, D. M., P. V. Roberts, and J. A. Cherry. 1985. Transport of organic contaminants in groundwater. Environ. Sci. Tech. 19:384-392.
34. Mangold, D. C., and C.-F. Tsang. 1991. A summary of subsurface hydrological and hydrochemical models. Rev. of Geophys. 29(1):51-79.
35. McCarty, P. L., B. E. Rittman, and E. J. Bouwer. 1984. Microbial processes affecting chemical transformations in groundwater. In: G. Bitton and C. P. Cerba (eds.), Groundwater Pollution Microbiology, pp. 90-115, John Wiley, New York, NY.
36. McLay, C. D. A., K. C. Cameron, and R. G. McLaren. 1991. Effect of time of application and continuity of rainfall on leaching of surface-applied nutrients., Aust. J. Soil Res. 29(l):l-9.
37. Miller, E. E., and R. D. Miller. 1956. Physical theory of capillary flow phenomena. J. Appl. Phys. 27:324-332.
38. Moench, A F. 1984. Double-porosity models for a fissured groundwater reservoir with fracture skin. Water Resour. Res., 20:831-846.
39. Molz, F. J. 1981. Models of water transport in the soil-plant system. Water Resour. Res. 17(5):1245-1260.
40. Nielsen, D. R., P. M. Tillotson, and S. R. Vieira. 1983. Analyzing field-measured soil-water properties. Agric. Water Manage. 6(1):93-109.
41. Nielsen, D. R., M. Th. van Genuchten, and J. W. Biggar. 1986. Water flow and solute transport processes in the unsaturated zone. Water Resour. Res. 22(9):89S-108S.
42. Omoti, U., and A. Wild. 1979. Use of fluorescent dyes to mark the pathways of solute movement through soils under leaching conditions, 1. Laboratory experiments. Soil Sci. 128(4):28-37.
43. Othmer, H., B. Diekkriiger, and M. Kutilek. 1991. Bimodal porosity and unsaturated hydraulic conductivity. Soil Sci. 152(3):139-150.
44. Persaud, N., J. V. Giraldez, and A. C. Chang. 1985. Monte-Carlo simulation of non-interacting solute transport in a spatially heterogeneous soil. Soil Sci. Soc. Am. J. 49(3): 562-568.

45. Peters, R. R., and E. A. Klavetter. 1988. A continuum model for water movement in an unsaturated fractured rock mass. Water Resour. Res. 24:416-430.
46. Pinder, G. F., and L. M. Abriola. 1986. On the simulation of nonaqueous phase organic compounds in the subsurface. Water Resour. Res. 22(9):109S-119s.
47. Pruess, K., and J. S. Y. Wang. 1987. Numerical modeling of isothermal and non-isothermal flow in unsaturated-saturated fractured rock - A review. In: D. D. Evans, and T. J. Nicholson (eds.), Flow and Transport Through Unsaturated Fractured Rock. pp. 1 l-22, Am. Geophys. Union, Washington, D.C.
48. Rhoades, J. M. 1994. Salinity assessment: Recent Advances and Findings. Trans. 15th Int. Congress of Soil Science, Int. Soil Sci. Soc., Acapulco, Mexico.
49. Richards, L. A. 1931. Capillary conduction of liquids in porous mediums. Physics 1:318-333.
50. Russo D., E. Bresler, U. Shani, and J. C. Parker. 1991. Analysis of infiltration events in relation to determining soil hydraulic properties by inverse problem methodology. Water Resour. Res. 27(6):1361-1373.
51. Sardin, M., D. Schweich, F. J. Leij, and M. Th. van Genuchten. 1991. Modeling the nonequilibrium transport of linearly interacting solutes in porous media: A review. Water Resour. Res. 27(9):2287-2307.
52. Schulin, R., M. Th. van Genuchten, H. Fluhler, and P. Ferlin. 1987. An experimental study of solute transport in a stony field soil. Water Resour. Res. 23(9):1785-1791.
53. Shouse, P. J., J. B. Sisson, T. R. Ellsworth, and J. A. Jobes. 1992. Estimating in situ unsaturated hydraulic properties of vertically heterogeneous soils. Soil Sci. Soc. Am. J. 56(6):1673-1679.
54. Simmons, C. S. 1982. A stochastic-convective ensemble -method for representing dispersive transport in groundwater. Report CS-2258, Electric Power Research Institute, Palo Alto, CA.
55. Šimůnek, J., and D. Suarez. 1994. Modeling unsaturated water flow, and CO_2 and solute transport with major ion chemistry. Trans. 15th Int. Congress of Soil Science, Int. Soil Sci. Soc., Acapulco, Mexico.
56. Smettem, K. R. J., and C. Kirby. 1990. Measuring the hydraulic properties of stable aggregated soil. J. Hydrol. 117:1-13.
57. Sposito, G., and W. A. Jury. 1985. Inspectional analysis in the theory of water flow through soil. Soil Sci. Soc. Am. J. 49(4):791-797.
58. Sposito, G., and R. J. Reginato. 1992. Opportunities in Basic Soil Science Research. Soil Sci. Soc. Am., Inc., Madison, WI.
59. Sposito, G., W. A. Jury, and V. K. Gupta. 1986. Fundamental problems in the stochastic convection-dispersion model of solute transport in aquifers and field soils. Water Resour. Res. 22(1):77-88.
60. Stevenson, F. J. (ed.). 1982. Nitrogen in Agricultural Soils. Agronomy No. 22, Am. Soc. Agron., Madison, WI.
61. Sudicky, E. A., and P. S. Huyakorn. 1991. Contaminant migration in imperfectly known heterogeneous groundwater systems. Rev. of Gcophys., Supplement 29:238-25 1.
62. Thoma, S. G., D. P. Gallegos, and D. M. Smith. 1992. Impact of fracture coatings on fracture/matrix flow interactions in unsaturated, porous media. Water Resour. Res. 28: 1357-1367.
63. van Dam, J. C., J. N. M. Stricker, and P. Droogcrs. 1990. From One-Step to Multi-Step Determination of Soil Hydraulic Functions by Outflow Measurements. Dept. of Water

Resources, Rep. No. 7, Agricultural University, Wageningen, The Netherlands.
64. van der Heijde, P. K. M. 1993. Identification and Compilation of Unsaturated/Vadose Zone Models. Robert S. Kerr Environ. Res. Laboratory, Office of Research and Development, U. S. Environ. Protection Agency, ADA, OK.
65. van Genuchten, M. Th. 1981. Non-Equilibrium Transport Parameters from Miscible Displacement Experiments. Research Report No. 119, U. S. Salinity Laboratory, USDA, ARS, Riverside, CA.
66. van Genuchten, M. Th. 1985. A general approach for modeling solute transport in structured soils. Proc. Int. Congress, Hydrageology of Rocks of Low Permeability, Jan. 7-11, Tucson, Arizona. Memoires Int. Assoc. Hydrogeol. 17(2):513-526.
67. van Genuchten, M. Th., and F. N. Dalton. 1986. Models for simulating salt movement in aggregated field soils. Geoderma 38:165-183.
68. van Genuchten, M. Th., and F. J. Leij. 1992. On estimating the hydraulic properties of unsaturated soils. In: M. Th. van Genuchten, F.J. Leij, and L. J. Lund (eds.), Proc. Int. Workshop on Indirect Methods for Estimating the Hydraulic Properties of Unsaturated Soils, pp. 1-14, University of California, Riverside.
69. van Genuchten, M. Th., D. E. Rolston, and P. F. Germann (eds.). 1990. Transport of Water and Solutes in Macropores. Special Issue, Geoderma 46(1-3):1-297.
70. Vogel, T., M. Cislerova, and J. W. Hopmans 1991. Porous media with linearly variable hydraulic properties. Water Resour. Res. 27(10):2735-2741.
71. Wagenet, R. J. 1983. Principles of salt movement in soil._ In: D. W. Nelson, D. E. Elrick, and K. K. Tanji (eds.), Chemical Mobility and Reactivity in Soil Systems, pp. 123-140, Publ. No. 11, Soil Sci. Soc. of Am., Madison, WI.
72. Wang, J. S. Y. 1991. Flow and transport in fractured rocks. Rev. of Geophys., Vol. 29, Supplement, pp. 254-262.
73. Wang, J. S. Y., and T. N. Narasimhan. 1985. Hydrologic mechanisms governing fluid flow in a partially saturated, fractured, porous medium. Water Resour. Res. 21:1861-1874.
74. Wheatcraft, S. W., and J. H. Cushman. 1991. Hierarchical approaches to transport in heterogeneous porous media. Rev. of Geophys., Vol. 29, Supplement, pp. 261-267.
75. White, R. E., J. S. Dyson, Z. Gerstl, and B. Yaron. 1986. Leaching of herbicides through undisturbed cores of a structured clay soil. Soil Sci. Soc. Am. J. 50:277-283.
76. Widdowson, M. A., F. J. Molz, and L. D. Benefield. 1988. A numerical transport model for oxygen- and nitrate-based respiration linked to substrate and nutrient availability in porous media. Water Resour. Res. 24(9):1553-1565.
77. Wilding, L. P., and C. T. Hallmark. 1984. Development of structural and microfabric properties in shrinking and swelling clays. In: J. Bouma and P. A. C. Raats (eds.), Proc. of the ISSS Symposium on Water and Solute Movement in Heavy Clay Soils, ILRI Publ. 37, pp. 1-18, Int. Inst. for Land Reclamation and Improvement, Wageningcn, The Netherlands.
78. Wood, E. F. 1991. Global scale hydrology: Advances in land surface modeling. Rev. of Geophys., Vol. 29, Supplement, pp. 193-201.
79. Zachmann, D. W., P. C. Duchatcau, and A. Klute. Simultaneous approximation of water capacity and soil hydraulic conductivity by parameter identification. Soil Sci. 134: 157-163.