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**-Characterization of Solute Transport in
Spatially-variable Unsaturated Field Soils**

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**CHARACTERIZATION OF SOLUTE TRANSPORT IN
SPATIALLY-VARIABLE UNSATURATED FIELD SOILS**

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BARD Project US-1484-88

ABSTRACT

This report focuses on the problem of solute transport through the unsaturated zone of heterogeneous field soil. Through a series of field studies and theoretical simulations, US and Israeli investigators developed and tested new stochastic descriptions of water and solute flow, which can be summarized in two categories: stochastic continuum modeling and transfer function modeling. The stochastic continuum approach was studied in a series of theoretical simulations of water and solute transport at both institutions, using field data from several sites to generate qualitative attributes of field scale transport. The stochastic continuum approach, although greatly restricted by its assumptions from representing processes in the vadose zone, nonetheless provided qualitative insight into phenomena observed and simulated in the field, and shows promise for quantitative representation of gravity-dominated flow in non-layered soils. In layered soils, transfer function modeling may be the only approach that can describe the complex processes occurring therein. This was demonstrated in a quantitative analysis of solute plume movement in field soil, and in adsorbing solute transport in columns taken from a field site. In each case, the non-mechanistic transfer function was the only recourse for describing the heterogeneous flow processes, because phenomena such as preferential flow cannot be simulated by existing models..

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INTRODUCTION

The study of chemical movement through unsaturated field soil has become increasingly important as concerns over groundwater contamination have risen. Part of the contamination may be attributed to surface spills or leaks from underground storage facilities, but still others result from natural application of chemicals to the land as a result of agricultural activities. Regardless of the source of contamination, these events have created a great impetus for the development of computational methods describing the water flow and chemical transport process in the unsaturated or vadose zone. Such methods are based on a conceptual framework, on subsequent theoretical developments, and ultimately on particular models that are adapted to the specific problem under study. The purpose of these developments is twofold: to improve the basic understanding of the transport process and to provide quantitative, predictive tools. In turn, these tools are used to predict the future spread of pollutants in near-surface geological environments, and for management purposes such as development of procedures to minimize the hazard of polluting underground water supplies. Although transport-related research in unsaturated soil occurs at a variety of scales, our interest in this proposal was on the field-scale of practical relevance to environmental pollution. One of the distinctive features of the porous medium viewed at this scale is the spatial heterogeneity of its properties affecting transport. The spatial heterogeneity of properties is generally of an irregular fashion and occurs on a scale which is not captured by laboratory samples or experiments. These features have a distinctive effect on the spatial distribution of solutes as a result of transport through heterogeneous porous medium.

To illustrate the type of heterogeneity one may encounter in the vadose zone at the field scale, Figure 1 presents measured soil properties from Bet-Dagan, Israel, reported in Russo and Bouton (1992). This figure shows contour lines of log transformations of two soil properties (saturated hydraulic conductivity, K_s , and pore-size distribution factor, α) that affect transport in the vadose zone. Evident from this figure is how irregular and erratic the spatial variations are of both properties at the field scale.

It is clear that such heterogeneity must affect flow and transport processes occurring through them. Such variability has been borne out in field observations of transport made in studies in the past.

Figure 2, reproduced from Schulín et al. (1987), displays contour lines for measuring chloride concentrations in the unsaturated zone of a layered field soil in Switzerland. Obviously, the chloride concentrations show considerable variability in the lateral and vertical direction, even though the solute pulse was applied in a spatially uniform manner.

The data shown in Figures 1 and 2 illustrate succinctly the problem we addressed in our field-scale proposal. How can one incorporate the spatial variability of soil properties into a predictive model for flow and transport at the field scale? This question was addressed in a number of different ways at the two research institutions during the three years of the BARD project, using as the experimental foundation for theoretical approaches several data sets obtained under distinctly different soil conditions.

SUMMARY OF RESEARCH FINDINGS PRIOR TO THE PROJECT

The most common approach used in the analysis of transport processes in the vadose zone has been to model water and solute transport by using macroscopic soil physical and chemical properties which vary in a deterministic manner, obey physical and chemical laws, and are expressed in the form of partial differential equations (PDE). In this approach, water flow is described by the Richards equation and transport of noninteractive, nonvolatile conservative solutes is described by the convection dispersion equation (CDE).

The physical parameters of the Richards equation are expressed in terms of the functional relationships between the soil water pressure head, h , hydraulic conductivity tensor, K , and water content, θ . In principle, the $h(\theta)$ relationships are hysteretic and depend in a complicated manner on whether the soil is drying or wetting. As for the solute transport, restricting ourselves to the simple case of a noninteracting conservative

solute only, the physical parameters of the CDE are the components of the dispersion tensor, $\underline{D}$, and of the vector of the average interstitial water flow velocity, $\underline{V}$. To solve these equations, it is usually assumed that the soil is rigid, isotropic and homogeneous, so that the $\underline{K}(\theta)$ tensor is described by a single-valued deterministic $K(\theta)$ function, and the $\underline{D}$ tensor reduces to the two principal components representing longitudinal and transverse dispersion (Bear, 1972; Bresler, 1975).

However, because of the inherent spatial variability of soil properties (e.g., Beckett and Webster, 1971; Nielsen, Biggar and Erh, 1973; Russo and Bresler, 1981; Jones and Wagenet, 1984, among others), the traditional deterministic approach used to analyze water and solute transport processes may be limited in its applicability to field-scale transport problems. Because of the randomly-varying (stochastic) nature of the transport parameters, $K(\theta)$, $h(\theta)$, and therefore of $\underline{V} = \underline{V}[K(\theta), h(\theta); BIC]$ and $\underline{D} = \underline{D}(\underline{V}; \lambda_L, \lambda_T)$ (where λ_L and λ_T are the longitudinal and transverse dispersivities, respectively, and BIC refers to the boundary and initial conditions), the soil system response (in terms of θ , h , or the solute concentration C) to a given set of BIC is also stochastic. This problem has led to the development of stochastic models to describe water and solute transport (Dagan and Bresler, 1979; Bresler and Dagan, 1981; Amoozegar-Fard et al., 1982; Jury, 1982; Simmons, 1982; Bresler and Dagan, 1983), and water flow (Dagan and Bresler, 1983; Andersson and Shapiro, 1983; Yeh, Gelhar and Gutjahr, 1985; Mantoglou and Gelhar, 1987).

The existing vadose-zone stochastic solute transport models differ in some of their underlying assumptions, boundary and initial conditions, and method of solution. They share, however, a common goal, namely, evaluation of the probability density function (PDF) of the solution concentration C as a function of time t , and soil depth z . In general, one can distinguish between mechanistic and non-mechanistic models. Mechanistic is taken here to imply that the model incorporates the most fundamental mechanisms of the process, as presently understood (for example, describing water flow by the Richards equation and solute transport by the CDE). Non-mechanistic implies that the model disregards the internal physical mechanisms which contribute to the transport process,

and concentrates on the relationships between an input function and an output response function.

THE MECHANISTIC APPROACH

In groundwater hydrology, the porous medium is visualized as being characterized by variations at two different scales (Gelhar, 1986). The larger-scale variations are viewed as slowly varying deterministic trends around which there are more localized variations which are viewed as locally stationary. The fundamental properties of the porous medium that affect local solute transport are regarded as a spatial random field, and a stochastic form of the governing PDEs is derived, in which random parameters are represented statistically. The solutions of these stochastic equations produce average macroscale transport predictions (Gelhar, 1986). These macroscale parameters are intrinsically related to the statistical parameters describing the complex three-dimensional heterogeneity of the hydraulic properties of the medium, with the relationship being determined from the solution of the stochastic equations. Examples of this approach for the case of complex-structured, three-dimensional groundwater systems were provided by Dagan (1982, 1984) and Gelhar and Axness (1983).

Initial efforts at stochastic modeling of unsaturated flow and solute transport in spatially-variable soils (Dagan and Bresler, 1979, 1983; Bresler and Dagan, 1981, 1983a,b) visualized the unsaturated flow system to be comprised of a collection of one-dimensional (vertical) independent soil columns with negligible interaction between columns. The typical horizontal dimension scale of these hypothetical soil columns was not specified. Each vertical column, however, was assumed to be vertically homogeneous (i.e., possible property variations with depth were neglected and depth-averaged values were used), so that flow and transport in each of these columns can be described by the one-dimensional vertical Richards equation and the one-dimensional vertical CDE, respectively. Accordingly, the variability in the response of the field results from variations in the soil properties among the vertical soil columns. However, if solute transport occurs to relatively large depths, say to a deep water table, the heterogeneity

of the soil properties in the vertical direction may influence the transport process. Therefore, it is important in such cases to evaluate the effect of the three-dimensionality of the soil property variations on the transport. The problem, however, is extremely complex and so far has not been studied in a theoretical framework except for a few investigations of water flow (Yeh et al., 1985; Mantoglou and Gelhar, 1987) which were restricted to the analyses of steady unsaturated and transient-unsaturated water flows, respectively, with vertical mean infiltration through an unbounded heterogeneous porous medium.

The models of Dagan and Bresler (1979, 1983a) and Bresler and Dagan (1979, 1981, 1983a,b) for the one-dimensional vertical transport of non-interacting solutes represent the stochastic mechanistic approach to analysis of field-scale solute transport in the vadose zone. Even though the results of their analyses are restricted by their simplifying assumptions (such as representing the spatial variations of the soil hydraulic properties in terms of a single variate, the scaling factor δ , which is assumed to be independent of its spatial position), they may be applicable to the upper part of the vadose zone. Their results suggested that the average concentration profile in a heterogeneous field cannot generally be modeled as the solution of the classical CDE with constant effective coefficients. This is so because in a heterogeneous field the position variance of the average concentration profile is dominated by lateral differences in vertical velocities and hence expands as the square of time, while in the solution of the CDE for an equivalent homogeneous fictitious soil, the position variance is dominated by dispersive mixing about a single average vertical flow velocity and hence expands proportional to time. In other words, their work demonstrated that under field conditions the dominant solute spreading mechanism is the spatial heterogeneity of the porous medium combined with convection.

NON-MECHANISTIC APPROACH

An alternative stochastic approach, non-mechanistic in form, is the transfer function model (TFM) applied to soils by Jury (1982). This approach assumes that the internal

physical mechanisms which contribute to the solute movement are unknown or unknowable. Therefore, the soil water system is characterized entirely in terms of its method of transforming an input function (solutes added to the soil surface) into an output function (solutes moving through the soil). According to this perspective, the movement of solute through the unsaturated zone is governed by a travel-time PDF $f_L(t)$, such that $f_L(t)dt$ gives the probability that a solute entering the soil surface ($z=0$) at time zero will reach the depth $z=L$ in the time interval between t and $t+dt$. If a noninteractive solute enters the soil surface in a spatially-uniform narrow pulse application (i.e., solute input occurs on a time scale very short compared to the observation time), $f_L(t)$ may be approximated by equating it with the average flux concentration (Parker and van Genuchten, 1984) measured at $z=L$. To predict solute transport beyond the measurement zone ($0 < z < L$), however, mechanistic assumptions are required. Under the assumption that convective vertical solute movement dominates lateral solute mixing, and that the profile is vertically homogeneous, the distribution of the physical processes contributing to the travel-time PDF $f_L(t)$ between $z=0$ and $z=L$, is the same for all depths, and the travel-time PDF $f_Z(t)$ for any arbitrary depth Z can be related to that for the reference depth L by the transformations (Jury, 1982)

$$f_Z(t) = L/Z f_L(Lt/Z) \quad (1)$$

Jury, Sposito and White (1986) generalized the TFM of Jury (1982) to describe the movement of solute that may undergo physical, chemical or biological transformations as it moves through the soil by introducing a solute lifetime PDF instead of the solute travel-time PDF. They showed that the generalized TFM may be derived from the law of mass balance for a solute as interpreted in the context of the probability theory. They concluded therefore that mechanistic stochastic models (MSM) of solute movement consistent with the law of mass balance are also consistent with the TFM of Jury (1982). For example, if the assumption is made that convective solute movement dominates lateral mixing, the TFM predicts that the variance of the travel time is proportional to the

square of the depth of observation, which means that the effective dispersivity will increase linearly with depth. This is consistent with the results of the MSM of Dagan and Bresler (1979), emphasizing the effect of the pore water velocity variations on solute spreading.

The consistency between the results of the TFM of Jury (1982) and the MSM of Dagan and Bresler (1979) is not surprising since both models assume that the transport process is dominated by lateral variations in vertical velocity. In addition, both models neglect possible depth variations of their input entities, and consider them as second-order "white noise" random stationary processes, independent of their spatial positions. Thus, possible correlations between nearby spatial points (characterized by a correlation scale) or the presence of an underlying drift, are ignored. Finally, both models neglect the higher dimensionality of the flow system and the possible effects of transverse fluxes and/or lateral solute mixing. With respect to the former, it should be noted that the scale effect (i.e., the increase in the effective field-scale dispersivity with travel time or travel distance from the source) predicted by these models, may be partially due to the fact that a higher dimensional process is modeled by a lower dimensional model (one-dimensional), as discussed by Domenico and Robbins (1984) and Robbins and Domenico (1985).

A significant difference between the two models is in that the TFM, the solute concentration variability is assessed directly by calibration of the travel time PDF, while in Bresler and Dagan's model the variability is assumed to arise from variations in water content induced by variable transport and retention properties. Thus, the TFM automatically includes all mechanisms contributing to solute flow variability while the MSM postulates candidate mechanisms for water flow variability. In that sense, the TFM incorporates higher dimensional effects while the MSM does not.

In dealing with the problem of field-scale convective solute transport, where the solute spreading is dominated by the spatial distribution of the pore water velocity, it is important to evaluate the effect of the correlation structure of the hydraulic properties and the higher dimensionality of the property variations on the water velocity field. One possible approach to this problem may be based on the study of Yeh et al. (1985), who

analyzed steady unsaturated water flow with vertical mean infiltration through unbounded heterogeneous porous media, using a perturbation approximation of the stochastic flow equation.

Although the analysis of Yeh et al. (1985) is restricted by some of its underlying assumptions (e.g., exponential $K(h)$ model, unbounded domain, and small perturbations), it points out a few general features of the flow regime in heterogeneous porous media. The most significant point is the effect of both correlation scale l_f of log K s and soil texture (in terms of α , the parameter of the $K(h)$ model) on the variability of the flow, and the trade-off between these two parameters. Accordingly, in fine-textured soils (small α), larger variability of the flow is expected, and the effect of the correlation scale on the flow is relatively small as long as its value is only a few meters. On the other hand, in coarse-textured soils (large α), smaller variability of the flow is expected, and the effect of the correlation scale to further reduce the flow variability may be significant even when its value is less than 1 m.

Inherent in the two approaches (as in all stochastic theories) is the ensemble concept for defining the statistical properties of the input parameters and the output variables. Consequently, the ergodic hypothesis (Lumley and Panofsky, 1964) must be invoked in order for the measurements which calibrate the models to be applicable to the entire field area. This hypothesis stated that inferences about statistical structure of a stochastic spatial function, $U(x)$ (where x is the vector of the spatial coordinates) may be based on estimates of the ensemble averages gained from spatial averages obtained from a single realization of $U(x)$. For the spatial averaging process to be meaningful, the spatial heterogeneity scale must be relatively small as compared with the overall scale of observation.

The analysis of Russo and Bresler (1982) suggested that in the case of a two-dimensional isotropic (in the horizontal plane of the field) second-order stationary function, $U(r)$ [where $r = (x_1^2 + x_2^2)^{1/2}$], the error in estimating the ensemble averages of $U(r)$, based on spatial averaging depends on both the coefficient of variation (CV) of $U(r)$, and on the correlation scale l of $U(r)$, relative to the typical length of the field. For example, for a soil property $U(r)$, characterized by $CV = 0.7$ and $l = 5$ m, more than 100

measurements should be made over an area equivalent to more than 100 correlation scales (i.e., 80 ha) in order to estimate the ensemble mean of $U(r)$ with 20% error.

OBJECTIVES OF PRESENT STUDY

The preceding overview represented the *status quo* in 1988 when the research project was initiated. At that time, existing models and field studies were far apart, and processes were incompletely understood. In the study reported below, we approached the field-scale problem from both a fundamental and a practical manner, building on the foundation of research generated previously in both Riverside and The Volcani Center, with the overall goal of formulating field-scale solute transport and water flow models that utilize measurable parameters and describe environmental processes of relevance to societal problems. The objectives stated in the original project proposal were as follows: 1) to assemble databases useful for developing and validating mathematical models of vadose zone transport of water and solutes, 2) to identify the processes controlling water and solute transport in spatially-variable unsaturated field soils, 3) to test whether local-scale measurements of soil, water and solute parameters can be used to predict field-scale transport, 4) to apply our understanding of field-scale spatial variability to practical problems relevant to management of soil water, soil salinity, and maintenance of environmental quality.

FIELD DATA SETS USED IN STUDY

Table 1 shows the eight field data sets used to obtain information for the modeling approaches followed in the study. Two of the data sets were obtained on research conducted during the study and the other six obtained from previous information either at the sites or used by research collaborators of the principal investigators.

In some cases, these data sets are used in actual simulation modeling, and in other cases display trends that are interpreted through simulation modeling.

The remaining material in this section is concerned with the modeling approaches used on these data sets. The results are divided between research conducted in Israel and research conducted in the U.S. At the end of the report the cooperation between the two institutes is presented in a separate section.

RESULTS OF ISRAELI RESEARCH

In subsurface hydrology, stochastic models of solute transport at the formation scale have been developed, based on a theoretical framework (e.g., Dagan, 1982, 1984; Gelhar and Axness, 1983). Unfortunately, these models have been restricted to saturated groundwater flow. Although the underlying physical bases of these systems are similar, groundwater transport and vadose-zone transport do differ with respect to the scale of the flow domain, the flow regime, and the direction of the principal flow components relative to porous formation strata. Theoretical developments in groundwater transport modeling have been facilitated by the fact that under steady flow (which is a reasonable approximation for the flow in aquifers), the only relevant flow parameter is saturated conductivity, K_s , which in turn is an inherent formation property. For the sake of completeness, the results obtained in the past by the theory of transport in groundwater that are relevant to the present analysis, will be reviewed briefly. For a comprehensive review, see e.g., Dagan (1987, 1989).

TRANSPORT IN SATURATED POROUS MEDIA

The theory is based on two distinct, independent stages. In the first stage, which is independent of whether the flow is saturated or unsaturated, the transport theory relates the spatial moments of the solute body to the velocity field. It is assumed that transport through a heterogeneous porous formation can be described as dispersion by

continuous motions (Dagan, 1989), as was first suggested by Taylor (1921). Implicit in the transport theory are the following assumptions:

- 1) Lagrangian and Eulerian stationarity and homogeneity,
- 2) given statistics of the velocity field,
- 3) negligible fluctuations of particle displacement about the mean trajectory.

Employing the aforementioned assumptions for Ergodic conditions, and neglecting pore scale dispersion, the first two moments of the PDF of the solute particle displacement can be expressed (Dagan, 1982, 1984) as:

$$\frac{d \langle \underline{X}(t) \rangle}{dt} = \underline{U} \quad (2a)$$

and

$$\frac{dX_{ij}(t)}{dt} = 2 \int_0^t C_{uu}(\underline{U}t') dt' \quad (2b)$$

where $\langle \underline{X}(t) \rangle$ is the expected value of the particle position (i.e., the average trajectory of the center of gravity of the solute body); $X_{ij}(t)$ ($i, j=1,2,3$) is the particle displacement covariance tensor (i.e., the average "moment of inertia" or second spatial moment of the solute body, with respect to its mean center of gravity); $\underline{U}$ is the expected value (assumed to be constant, and uniform in time and space) of the Eulerian velocity field, $\underline{v}(\underline{x}, t)$, which in turn is assumed to be time-independent; and $C_{uu}(\underline{s}) = \langle \underline{u}(\underline{x}_1) \underline{u}(\underline{x}_2) \rangle$ is the velocity covariance function, where $\underline{s} = \underline{x}_1 - \underline{x}_2$ is the separation vector, and $\underline{u}(\underline{x}, t)$ the velocity fluctuation. Once the velocity field has been determined, either by measurement or by computation, so that the first two moments of the joint PDF of the velocity field are estimated, the first two spatial moments of the solute body, $\langle \underline{X}(t) \rangle$ and $X_{ij}(t)$, can be evaluated from Eqs. (2a) and (2b), respectively. The latter is related directly to the macrodispersion tensor, D_{ij} (Smith and Schwartz, 1980; Dagan, 1981, 1984; Gelhar and Axness, 1983).

The second stage, which is independent of the flow regime, consists of relating the statistical moments of the velocity field to the moments of the properties of the heterogeneous formation. For saturated groundwater flow, this task has been accomplished (Dagan, 1982, 1984; Gelhar and Axness, 1983; Neuman et al., 1987) using Darcy's law and the continuity equation for water flow. In these studies, it was assumed that the porosity, ϕ , of the heterogeneous formation is constant and deterministic, whereas the other relevant formation property, saturated conductivity, K_s , is stationary and log-normally distributed, and characterized completely by the expected value F of $\log K_s$ and by the covariance function $C_{ff}(\underline{s})$ of the fluctuation of $\log K_s$. For a domain of large extent, compared with the correlation scale of $\log K_s$, l_f , for a uniform average head gradient, $\underline{J}(J_1, 0, 0)$, and by an analysis to first-order in $\sigma_f^2 = C_{ff}(0)$, expressions for the mean velocity, $\underline{U}$, and the velocity covariance, $C_{uu}(\underline{s})$, in terms of F and $C_{ff}(\underline{s})$, were obtained in the past (see, e.g., Dagan, 1984):

$$\underline{U} = \underline{J}K_G/\phi \quad (3a)$$

$$C_{uu}(\underline{s}) = \underline{U}^2 C_{ff}(\underline{s}) + B \quad (3b)$$

Here, $K_G = e^{<F>}$ is the geometric mean of K_s , whereas the additional nonwritten terms denoted by B in (3b) are given elsewhere (Dagan, 1984).

Combining the two aforementioned stages, Dagan (1984) derived closed-form analytical expressions for the longitudinal (X_{11}) and the transverse (X_{22}) components of the ensemble time-dependent displacement covariance tensor for a tracer solute moving through a heterogeneous, infinite aquifer with an isotropic structure under two- and three-dimensional, steady-state, saturated flows, in terms of the variance, σ_f^2 , and the correlation scale l_f of the input formation property, $\log K_s$. Later Dagan (1988) extended the theory to a more generalized case, considering flow and transport through heterogeneous anisotropic structures. The components of the time-dependent ensemble displacement covariance tensor derived from Dagan's (1984) model compared favorably

with those obtained from an analysis of the temporal behavior of the spatial moments of the tracer plume at the Borden site (Freyberg, 1986; Sudicky, 1986).

TRANSPORT IN UNSATURATED POROUS MEDIA

Water flow in the vadose zone (which might be transient and nonmonotonic as well), is much more complicated than groundwater saturated flow. In this case, the relevant flow parameters - hydraulic conductivity, K , and water capacity, C - depend both on formation properties (e.g., saturated conductivity, pore size distribution, and saturated and residual water contents) and on dependent flow variables - water saturation, S , or capillary pressure head, ψ - in a highly nonlinear fashion. Consequently, under saturated flow, evaluation of the effects of variations of the porous medium properties on transport is extremely complex, and so far has not been studied in a theoretical framework - except for a few investigations of water flow, based on a small perturbation approximation of a stochastic, linearized flow equation (Yeh et al., 1985a,b; Mantoglou and Gelhar, 1987a,b,c). Moreover, these studies were restricted to analyses of steady unsaturated, and transient unsaturated water flows, respectively, of vertical mean infiltration through an unbounded, infinite, heterogeneous porous medium.

SIMULATION OF SOLUTE TRANSPORT

Simulation is a powerful tool that can be regarded as a "numerical experiment", which in turn can provide much more detailed information (which is unaffected by uncertainty due to measurement errors or inadequate sampling) about the effects of spatial variability in soil properties on the response of the flow system than is attainable in practice from field investigations. Furthermore, results of transport simulations may be used to test the applicability of current stochastic vadose-zone transport models to more realistic field situations.

The problem of transport of a conservative, nonreactive solute in a vertical cross-section of a hypothetical, partially-saturated, heterogeneous soil under transient water flow, was simulated during the first project year (Russo, 1991). The simulation was based on the assumption that at the local scale, water flow and solute transport can be

described by the Richards equation and by the convection-dispersion equation (CDE), respectively. Furthermore, we employed the assumption of scale-heterogeneity (Philip, 1967), so that the logarithm of the scaling factor, $Y = \log \delta$, was considered to be a realization of a random field characterized by an anisotropic, axisymmetric, two-dimensional exponential covariance function.

The movement of a single chloride pulse in the vertical cross-section of the hypothetical, but realistic, heterogeneous soil was simulated for 34 days under a transient flow regime generated by daily irrigations. Simulated water content and solute concentration distributions in the vertical cross-section of the heterogeneous soil at different times were quantified in terms of space averages and covariance functions. Time-evolution of the solute plume was quantified in terms of its first two spatial moments, from which the time-dependence of the longitudinal and the transverse components of the velocity vector and the spatial covariance tensor were estimated. The simulated transport and the accompanying analysis (Russo, 1991) were based on single realizations of the formation input property, as well as of the output variables. It was assumed, therefore, that ergodicity requirements were at least partially satisfied. This was justified in view of the size of the solute inlet zone (which extended over 12 correlation scales of the input property formation, $\log \delta$, in the transverse horizontal direction), and the vertical extent of the domain where flow took place (over several tens of the correlation scale of $\log \delta$ in the longitudinal vertical direction), that ensured solute spread over a sufficiently large volume. Hence, an interchange between the concentration spatial moments and their ensemble mean was assumed, although the estimated value of the latter might be affected by uncertainty due to the finiteness of the solute inlet zone (Dagan, 1990).

Results of the simulated transport (Russo, 1991) are depicted in Fig. 3, and demonstrate the considerable variability in the solute concentration in space and time due to the complex heterogeneity of the soil hydraulic properties in both the vertical and the horizontal directions, in agreement with field data (see Fig. 2, data from Schulin et al., 1987). Because of the complex heterogeneity of the soil hydraulic properties, the movement of the simulated solute plume was characterized by a compression-expansion phenomenon. This is illustrated by the time-behavior of the longitudinal component of the

spatial covariance tensor (Fig. 4a) and the related longitudinal macrodispersion coefficient (Fig. 4b), derived from the spatial moment analysis of the simulated solute plume. These time-fluctuations are in qualitative agreement with field data (see Fig. 5, data from Ellsworth, 1989).

The components of the time-dependent spatial covariance tensor, obtained from the analysis of the temporal behavior of the spatial moments of the simulated solute plume in unsaturated flow, compared favorably with the components of the ensemble spatial covariance tensor derived from Dagan's (1984) model for transport by saturated groundwater flow (Fig. 4a). The momentary discrepancy between the actual spread of the single plume, and the one based on the ensemble-average of the solute body, was explained by the finiteness of the solute inlet zone (Dagan, 1990), and by the unsteadiness and the compressibility of the unsaturated flow (as compared with the constant-porosity, incompressible, steady, saturated flow). In addition, it was found (Russo, 1991) that the time-dependent longitudinal macrodispersivity, λ_{11} , determined from depth moment integrals of the depth-scaled, one-dimensional CDE (Jury and Sposito, 1985), using horizontally averaged concentrations, was in qualitative agreement with $\lambda_{11}(t)$ determined from the stochastic groundwater transport model of Dagan (1984) (Fig. 4b). Furthermore, the asymptotic of $\lambda_{11}(t \rightarrow \infty) = 3.47$ cm (Russo, 1991) was in very good agreement with the asymptotic value of the longitudinal component of the macrodispersivity tensor derived by Dagan (1982, 1984) and also by Gelhar and Axness (1983) for two- and three-dimensional saturated, steady flows, as:

$$\lambda_{11}(t \rightarrow \infty) = D_{11}(t \rightarrow \infty)/U_1 = \sigma_f^2 l_{fz} \quad (4)$$

where U_1 and D_{11} are the longitudinal components of the mean velocity vector, and the dispersion tensor, respectively, in the vertical direction, and $\sigma_f^2 = \langle f'^2 \rangle$ and l_{fz} are the variance and the correlation scale, respectively, in the longitudinal direction of the input formation property, $\log K_s$. For the scale-heterogeneous soil analyzed here, $\sigma_f^2 = 0.29$, and $l_{fz} = 12$ cm, and hence from (4), $\lambda_{11}(t \rightarrow \infty) = 3.48$ cm.

Based on the analysis of the first two spatial moments of the simulated solute plume, it was concluded (Russo, 1991) that the simplified, stochastic vadose-zone transport models (e.g., Dagan and Bresler, 1979; Jury, 1982), which predict that the variance of the travel distance is proportional to the square of the time of observation, may be applicable to relatively shallow depths ($\approx 1.8\text{m}$, or about 15 correlation scales of the input formation property in the longitudinal vertical direction). However, these simplified transport models may fail to describe the spread of a solute plume when the transport takes place to relatively great depths, mainly because of the neglect of vertical heterogeneity in the soil hydraulic properties, and of the higher dimensionality of the flow system, as well as possible effects of transverse fluxes and/or lateral solute mixing. These conclusions are supported in part also by the field data of Ellsworth (1989) (Fig. 5).

The surprising agreement between the effective dispersion in the simulated transport of Russo (1991) in unsaturated flow and previous theoretical developments in saturated flow (e.g., Dagan, 1984) (see Fig. 4) was explored in the second project year (Russo and Dagan, 1991) in a general Lagrangian formulation, by using small-perturbation, first-order approximations. The results of the analysis of the velocity field in the unsaturated flow domain of the hypothetical scale-heterogeneous soil (Russo, 1991) suggested good agreement between the result of the Lagrangian kinematic analysis and the result of the analysis of the spatial moments of the concentration distribution, in agreement with the stochastic theory of transport in saturated flow. This was explained by the finding that the product of the conductivity variance and its correlation scale (and, concurrently, the product of the velocity variance and its correlation scale), was of similar magnitude for both saturated and unsaturated flow regimes. Results of the analysis (Russo and Dagan, 1991) suggested that despite the complexity of unsaturated flow, as compared with saturated flow, it might be amenable to a similar analysis. They emphasized, however, that the question, of whether this contribution is a result of general validity, or rather a particular one pertaining to flow conditions in the simulation (Russo, 1991), should be investigated further.

STOCHASTIC MODELING OF SOLUTE TRANSPORT

A stochastic transport model was developed during the third project year (Russo, 1992) and might lead to a simple formulation of transport in unsaturated, heterogeneous soils. The development of this stochastic transport model was motivated by the recognition that the Lagrangian kinematic analysis, which describes the dependence of the particle displacement covariance tensor on the velocity covariance function and travel time [Eq. (2)], is of a general nature and applies to saturated and unsaturated flows as well (Russo and Dagan, 1991). Hence, the framework and results developed in the past for groundwater flow (see e.g., Dagan, 1989) can be adopted for analyzing vadose zone transport. This task was accomplished by combining a general Lagrangian formulation, relating the spatial moments of the solute body to the velocity field [Eq. (2)], with the stochastic theory of Yeh et al. (1985a,b) for steady, unsaturated flow, relating the statistical moments of the velocity field to those of properties of the heterogeneous formation.

The stochastic model considers transport of a conservative, nonreactive solute through a three-dimensional, heterogeneous, porous formation with an anisotropic structure, under unidirectional vertical, steady, unsaturated flow. In addition to the assumptions implicit in the Lagrangian kinematic analysis outlined above, the following assumptions were adopted:

- 1) At the core scale, the relations between conductivity, K , and the capillary pressure head, ψ , at a given point of the spatial coordinate system, $\underline{x}$, are isotropic, and can be described by the expression of Gardner (1958), i.e., $K(\psi, \underline{x}) = K_s(\underline{x})\exp[-\alpha(\underline{x})\psi]$.
- 2) The intrinsic formation properties, K_s and α , as well as the dependent flow variable, ψ (considered as a positive quantity), are second-order stationary random functions, and are ergodic over the region of interest.
- 3) The covariance functions of both $\log K_s$ and α are described by the three-dimensional, statistically anisotropic exponential function.
- 4) At the core scale, Darcy's law for unsaturated flow is valid.
- 5) For a given mean pressure head, H , the volumetric water content effective for water flow, θ_e , is constant and uniform in space.

By employing the aforementioned assumptions, expressing the velocity in terms of mean $\underline{U}$ and perturbation $\underline{u}$ utilizing Taylor's expansion, and by retaining first-order terms, expressions for the components of the velocity covariance in the direction of the mean expression gradient, i.e., $\langle u_1(\underline{x})u_1(\underline{x}') \rangle$

$$C_{u_1 u_1}(\underline{x}, \underline{x}') = \left[\frac{K_m}{\theta_e} \right]^2 \left[J_1^2 C_{yy}(\underline{x}, \underline{x}') + 2J_1 C_{yj_1}(\underline{x}, \underline{x}') + C_{j_1 j_1}(\underline{x}, \underline{x}') \right] \quad (5a)$$

and in the direction perpendicular to the mean gradient, i.e., $\langle u_2(\underline{x})u_2(\underline{x}') \rangle$

$$C_{u_2 u_2}(\underline{x}, \underline{x}') = \left[\frac{K_m}{\theta_e} \right]^2 \left[C_{j_2 j_2}(\underline{x}, \underline{x}') \right] \quad (5b)$$

were obtained (Russo, 1992). Here, $K_m = \exp(Y)$ is the geometric mean of unsaturated conductivity K ; $\theta_e = \theta_e(\psi)$ is the volumetric water content effective for water flow; $J_1 = -\partial(H + x_1)/\partial x_1$ is the mean hydraulic gradient in the vertical direction, x_1 ; and $C_{yy}(\underline{x}, \underline{x}') = C_{yy}(\underline{s})$ is the covariance function of log-unsaturated conductivity perturbation, given by:

$$C_{yy}(\underline{s}) = C_{ff}(\underline{s}) + H^2 C_{aa}(\underline{s}) + A^2 C_{hh}(\underline{s}) - 2AC_{fh}(\underline{s}) + 2AHC_{ah}(\underline{s}) \quad (6)$$

where A is the mean value of α ; $C_{ff}(\underline{s})$ and $C_{aa}(\underline{s})$ are covariance functions of the perturbation of the formation properties; $\log K_s$ and α , respectively; $C_{hh}(\underline{s})$ is the covariance function of the capillary pressure head perturbation; $C_{fh}(\underline{s})$ and $C_{ah}(\underline{s})$ are cross-covariance functions between perturbations of $\log K_s$ and ψ , and α and ψ , respectively; and $C_{yj_1}(\underline{x}, \underline{x}') = C_{yj_1}(\underline{s})$ is the cross-covariance function between perturbations of log-unsaturated conductivity and the capillary pressure head gradient in the x_1 direction ($j_1 = \partial h / \partial x_1$) given as:

$$C_{yj_1}(\underline{s}) = C_{fj_1}(\underline{s}) - HC_{aj_1}(\underline{s}) \quad (7)$$

where $Cf_{j_1}(\underline{s})$ and $Caj_1(\underline{s})$ are cross-covariance functions between perturbations of $\log K_s$ and j_1 , and α and j_1 , respectively; $Cj_1j_1(\underline{x},\underline{x}') = Cj_1j_1(\underline{s})$ and $Cj_2j_2(\underline{x},\underline{x}') = Cj_2j_2(\underline{s})$ are covariance functions of the capillary pressure gradient perturbations in the direction of the mean gradient, and perpendicular to the mean gradient, respectively.

Details of the evaluation of the various covariance and cross-covariance functions required to calculate the covariance functions of the components of velocity in the longitudinal vertical $[u_1(x_1)]$ and in the transverse lateral $[u_2(x_2)]$ directions from (5) are given elsewhere (Russo, 1992). By using the covariance functions of $u_1(x_1)$ and $u_1(x_1)$, and Eq. (2b), we estimated the respective components of the particle displacement covariance tensor ($X_{11}(t)$ and $X_2(t)$, respectively), and investigated effects of statistical properties of the relevant formation properties, $\log K_s$ and α (i.e., σ_f^2 , σ_a^2 , l_{fz} , l_{az} , $\rho_f = l_{fx}/l_{fx}$, and $\rho_a = l_{ax}/l_{az}$), as well as of the flow-dependent variable (i.e., mean capillary pressure head or mean water saturation) on both longitudinal and transverse components of the solute body spread.

The dependence of the dimensionless components of the displacement covariance tensor, $X'_{11} = X_{11}/l_{fz}\sigma_f^2$ and $X'_{22} = X_{22}/l_{fz}\sigma_f^2$, and the ratios $X'_{11}/2t'$ and $X'_{22}/2t'$, upon dimensionless travel time, $t' = tU_{11}/l_{fz}$, for a few values of the effective water saturation, S_e , is illustrated in Figs. 6 and 7, respectively. For purposes of comparison, the closed-form analytical expressions for $X'_{11}(t')$ and $X'_{22}(t')$, and for ratios $X'_{11}/2t'$ and $X'_{11}/2t'$, derived by Dagan (1984) for steady, three-dimensional flow in an isotropic, saturated porous formation, are also depicted in these figures. It should be emphasized that from a physical point of view, the ratios $X'_{11}/2t'$ and $X'_{22}/2t'$ may be regarded as apparent dispersion coefficients that would lead, in the solution of the convection-dispersion equation, to the same X_{11} and X_{22} as the actual time-dependent ones (Dagan, 1988). For $t \rightarrow \infty$, these ratios tend to the constant macrodispersion coefficients (Aris, 1956) defined as $D_{ii} = (1/2)(dX_{ii}/dt)$ ($i=1,2$, no sum on i).

As shown in Fig. 6, the dimensionless longitudinal $X'_{11}(t')$ and transverse $X'_{22}(t')$ components of the displacement covariance tensor calculated for the unsaturated, heterogeneous porous formation (Russo, 1992), are in agreement with the expressions derived by Dagan (1984) for saturated, heterogeneous porous formations. However,

water saturation affects both the magnitude and time behavior of $X'_{11}(t')$ and $X'_{22}(t')$. For a given dimensionless travel time, t' , as water saturation decreases, both X'_{11} and X'_{22} increase, the extent to which depending on the magnitude of the statistical parameters of the formation properties, $\log K_s$ and α . In addition, as water saturation decreases, both $X'_{22}(t')$ and $d(X'_{11}/dt')$ tend asymptotically to constant values more slowly. Generally, for a given water saturation, both $X'_{11}(t')$ and $X'_{22}(t')$ increase as the variability in both formation properties, $\log K_s$ and α , increases and as the ratio between the correlation scales of $\log K_s$ and α decreases. On the other hand, $X'_{11}(t')$ is essentially robust to the statistical anisotropy of the porous formation (expressed in terms of the aspect ratio, $\rho = l_f/l_{f1}$), while $X'_{22}(t')$ increases and tends asymptotically to constant values slower, as ρ increases, in agreement with the findings of Dagan (1988) for saturated flow.

It was shown (Russo, 1992) that in cases where the correlation scale l_f of $\log K_s$ is large, compared with the correlation scale l_a of α , the effect of water saturation on $X_{11}(t')$ is considerably smaller than its effect on $X'_{22}(t')$ (Fig. 6). The relative robustness of the longitudinal component $X'_{11}(t')$ (and concurrently, of the asymptotic constant longitudinal macrodispersion coefficient, $D_{11} = (dX'_{11}/dt')_{t \rightarrow \infty}$) to water saturation was explained by the fact that in cases where $l_f \gg l_a$, an increase in the variance of $\log K$ (and concurrently in the velocity variance) as water saturation decreases, is compensated in part by a decrease in the correlation scale of $\log K$ (and concurrently in the correlation scale of the longitudinal component of the velocity). In other words, in cases where $l_f \gg l_a$, the product of the variance and the correlation scale of long-conductivity, for both saturated and unsaturated conditions, are of similar magnitude, i.e., $\sigma_y^2 l_{y1} \approx \sigma_f^2 l_{f1}$, so that the constant longitudinal macrodispersivity coefficient $D_{11}/U_1 = \sigma_f^2 l_{f1}$ is of similar magnitude for both saturated and unsaturated conditions (Fig. 7). In cases where $l_f \leq l_a$, however, the product of $\sigma_y^2 l_y$, and concurrently the value of D_{11}/U_1 increases considerably as water saturation decreases.

Experimental data on the spatial variability in α are few and sparse. However, results of a recent field study at Bet Dagan (Russo and Bouton, 1992), based on 417 undisturbed soil cores taken from a vertical cross-section (20 m long and 2.5 m deep, see Fig. 1),

suggested that the estimated correlation scales of $\log K_s$ in both the vertical and horizontal directions were approximately three times larger than the respective correlation scales of α . In view of the analyses of vadose zone transport (Russo, 1991; Russo and Dagan, 1991) and the results of the stochastic analysis (Russo, 1992) presented here, this experimental information is encouraging in the sense that it supports further the conclusion that the spread of solutes in real, unsaturated, heterogeneous porous formations might be amenable to a relatively simple analysis.

RESULTS OF U.S. INVESTIGATIONS

The U.S. investigation focused on the application of transfer function modeling to the description of processes occurring at the field scale. A subset of this investigation was the study of rate processes occurring during chemical transport and interaction with soil solid phases. A final section of the U.S. study dealt with the analysis and interpretation of common macroscopic methods for measuring transport and flow properties under field conditions. Results of these studies are described below.

CHEMICAL TRANSPORT IN LAYERED SOIL

This field study, reported in Roth et al. (1991) consisted of a field experiment in which a chloride tracer was applied to the surface of a vegetable field and then leached downward by rainfall and irrigation. The experimental site was located near Zurich, Switzerland, near a field used for intensive vegetable production. Annual precipitation in this region is about 1,000 mm with maximum rates exceeding 100 mm per day during heavy rainstorms. Eight horizons of different textures can be distinguished in the soil profile of this field down to a depth of 3 m. The top 0.2 m of soil are thoroughly mixed by frequent plowing and cultivation. The position and thickness of the other layers vary as a consequence of the soil formation, which is characterized by illuviation and occasional hang slides. The soil texture down to about 1.6 m gradually changes as the clay content increases from 19 to 30%, while the sand content decreases from 46 to 38%. Stone

content is high between 1.4 and 2.25 m, occupying between 24 and 35% of the total volume. For this experiment a tunnel 12 m long, 2 m wide and 2.4 m high was constructed under the vegetable field, with the top of the access tunnel located approximately 0.6 m below the surface. From this tunnel, 110 solution sampler cups and 99 tensiometers plus eight time domain reflectometry probes were installed horizontally into a vertical measuring region. The zone of intense monitoring was about 10 m long and extended from 0.4 to 2.5 m below ground.

During the tracer experiments, the field above the measuring region was bare. The chloride tracer was applied uniformly to the surface at an aerial density of $5.6 \text{ mol Cl m}^{-2}$. to prevent boundary effects, the area over which solute was applied was extended beyond the measuring region by at least 3 m. Within 5 days the salts were completely dissolved by a total of 6 mm of rainfall and dew, creating a shallow initial resident concentration at the surface. The chloride pulse was subsequently leached downward by rainfall and irrigation. Cumulative infiltration was measured with three rain collectors that were read at the time when samples of the soil solutions were taken. Rainfall intensities were monitored with an automatic rain gauge. The infiltration during the experiment, a total of 853 mm, may be divided into three phases. During the first phase, 99 mm of rainfall infiltrated into the soil. In the second phase, a sprinkler system was installed to simulate heavy, continuous rainfall. The intensity of this stage was held constant during every single irrigation cycle but varied between cycles from 4 to 8 mm per hour. A total of 601 mm of water were applied in ten cycles during this stage. After this irrigation, the sprinkler system was removed. In the final phase, an additional 153 mm of water infiltrated as rainfall during the remainder of the experiment.

Chloride concentrations in the soil solution, water potentials and volumetric water contents were measured at regular intervals ranging from 1 to 15 days, depending on the cumulative infiltration.

Results

Horizontally Averaged Concentrations. An overview of the experimental results may be obtained by plotting horizontally averaged concentrations versus cumulative infiltration

(Figure 8). The averaging was done by applying a linear filter to the measured concentrations. This filter assigns to each measured concentration $c(x, z', l)$ at the position (x, z') after infiltration l , a weight $w_p(z-z')$ that depends on the distance of the suction cup from the depth z at which the average concentration is estimated.

The average concentration $\bar{c}(z, l)$ is then defined as the weighted sum of the measured concentrations, divided by the sum of all weights to get an unbiased estimate. This may be written as

$$\bar{c}(z, l) = \frac{\sum w_p(z-z') c(x, z', l)}{\sum w_p(z-z')} \quad (8)$$

where the sums extend over all positions (x, z') of the suction cups. We have chosen the hat-shaped weighting function

$$\begin{aligned} w_p(z) &:= 1 - |z|/p & |z| \leq p \\ w_p(z) &:= 0 & |z| > p \end{aligned} \quad (9)$$

with the range p equal to the mean vertical distance between the suction cups, i.e., $p = 0.2$ m.

Figure 8 shows that the single pulse of tracer split into a slowly-moving main pulse, plus a succession of fast pulses. By the end of the experiment, after 0.853 m of water had infiltrated, the maximum concentration of the slowly-moving pulse was located at a depth of about 0.84 m.

Contrasting with this slow pulse are the faster ones, which occurred sporadically and caused the background concentration at 2.2 m to increase by an order of magnitude after a total infiltration of 0.15 m. They moved rapidly to a depth of about 2.2 m, where they appeared to get "trapped" and there become diluted without further vertical movement.

In the middle layers of the measuring region, between 1 and 1.8 m, the concentration increased only gradually as the leading edge of the slow pulse encroached into this region.

Small Amounts of Infiltration. Parts of the tracer mass reached great depths after only a small amount of infiltration. This is illustrated by the spatial distribution of chloride for the early stages of the experiment (Figure 9). The natural precipitation following the application of the tracer had a very low intensity ($<4 \text{ mm h}^{-1}$). This dissolved the salts without leaching them deep into the soil, and after an infiltration of 13 mm the concentrations in the measuring region were still at the background level measured before the tracer was applied. However, during the following six days, 18 mm of rainfall infiltrated, with 10 mm in one hour during a rainstorm. While most concentrations remained at background levels, some of the deeper locations showed increases by more than an order of magnitude. This phenomenon also occurred later during high-intensity infiltrations.

Large Amounts of Infiltration. Although traces of the fast pulses remained detectable in the deeper layers of the profile, the tracer distributions after large amounts of infiltration mainly show the movement of the slow pulse (Figure 10). Despite the uniform application of the tracer to the soil surface, the pulse broke up into several disconnected plumes. This may be the result of a velocity field that contains horizontal convergence zones.

Analysis

The temporal and spatial resolution of this experiment was not high enough to yield reliable data about the fast pulses. In this section, we will therefore only consider the slowly-moving part of the tracer.

In the following analysis, we will consider two contrasting assumptions about the homogeneity of transport through the slower moving soil matrix on the transport scale: (1) the soil is homogeneous, which implies that solute transport may be described as a convection-dispersion process, and (2) the soil is homogeneous along the flow and inhomogeneous perpendicular to it. The second model may be described as a set of homogeneous stream tubes and leads to a stochastic-convection representation for the solute transport (Jury and Roth, 1990).

To model the experiment, we make the following major simplifying approximations:

1. The soil is homogeneous on the observation scale. This implies that solute movement is one-dimensional and that the local parameters of solute transport models are constant in space.
2. The form of the transport volume is constant. Together with the rather weak assumption that molecular diffusion may be neglected on the field scale, this implies that local parameters of solute transport models are constant when time is replaced by cumulative infiltration.

We approximate the initial condition of the experiment by a resident pulse at the surface. The samples extracted with the suction cups are assumed to represent resident concentrations in the liquid phase, which seems to be a reasonable approximation because the samples are extracted under high suction during a short time.

Convection-Dispersion Model

The dynamics of the one-dimensional steady-state convection-dispersion process can be described by

$$\frac{\partial}{\partial t} C_l^r = -V \frac{\partial}{\partial z} C_l^r + D \frac{\partial^2}{\partial z^2} C_l^r, \quad (10)$$

where $C_l^r [ML^{-3}]$ is the resident concentration in the liquid phase, i.e., the mass of tracer in a physically infinitesimal volume divided by the volume of liquid in this volume, $V [LT^{-1}]$ is the pore water velocity, and $D [L^2T^{-1}]$ is the dispersion coefficient (Nielsen and Biggar, 1962).

The cumulative infiltration I is defined by

$$I(t) = \int_0^t j_w(Y) dY, \quad (11)$$

where $j_w[LT^{-1}]$ is the water flux at the soil surface, and by approximation 2, also within the soil. The water flux j_w and the pore water velocity V may be used to define the apparent volume fraction $\varphi[L^3L^{-3}]$ of the soil through which solute transport occurs,

$$\varphi = j_w(t)/V(t) \quad (12)$$

Different field-scale phenomena, like a locally three-dimensional flow field or preferential flow, cause the value of φ to be smaller than the volumetric water content θ of the soil. We will therefore employ (12) to correspond to an apparent volumetric water content.

Under steady-state conditions, (11) reduces to

$$l(t) = j_w t, \quad (13)$$

which transforms (10) into

$$\frac{\partial}{\partial l} C_l^r = \frac{1}{\vartheta} \frac{\partial}{\partial z} C_l^r + \frac{\lambda}{\vartheta} \frac{\partial^2}{\partial z^2} C_l^r, \quad (14)$$

where $\lambda := D/V [L]$ is the dispersivity. We will use the solution of (14) obeying the boundary conditions

$$\left(\frac{1}{\vartheta} C_l^r - \frac{\lambda}{\vartheta} \frac{\partial}{\partial z} C_l^r \right) \Big|_{z=0} = 0, \quad \lim_{z \rightarrow \infty} C_l^r(z, l) = 0, \quad (15)$$

and the initial condition

$$C_l^r(z, 0) = (m_0/\theta) \delta(z) =: C_0 \delta(z), \quad (16)$$

where $m_0[ML^{-2}]$ is the mass density of the tracer that was applied to the soil surface to create the initial distribution, θ is the volumetric water content, $\delta(z)$ is Dirac's delta function (Arfken, 1985), and $C_0 := m_0/\theta$ is introduced to keep the notation concise.

In writing (16), we assumed that the applied tracer is uniformly dissolved in the entire water phase. Considering the low infiltration rates at the beginning of the experiment, this assumption seems reasonable.

The solution of (14)-(16), which may be obtained by applying the Laplace transform to the time and the space variables (Jury and Roth, 1990, Problem 3.8), may be written as

$$C_1^r(z, l) = C_0 \left[\left(\frac{\vartheta}{\pi \lambda l} \right)^{1/2} \exp\left(- \frac{(l - \vartheta z)^2}{4 \vartheta \lambda l} \right) - \frac{1}{2\lambda} \exp\left(\frac{z}{\lambda} \right) \operatorname{erfc}\left(\frac{l + \vartheta z}{2(\vartheta \lambda l)^{1/2}} \right) \right], \quad (17)$$

where $\operatorname{erfc}(\)$ is the complementary error function (Abramowitz and Stegun, 1970).

Stochastic-Convection Model

For a stochastic-convection process with the initial and boundary conditions given by (15)-(16), the mean concentration at the observation scale is

$$C_1^r(z, t) = \int f_p(p) C_1^r(z, t; p) dp, \quad (18)$$

where $C_1^r(z, t; p)$ is the concentration in a single stream tube described by the parameters p , $f_p(p)$ is the probability density function ~ (pdf) of the model parameters for the entire set of stream tubes, and the integration extends over the entire domain of p (Jury and Roth, 1990). For the sake of simplicity, we assume that the concentration within a stream tube may be described by a pure convection process, which leads to

$$C_1^r(z, t; V) = C_0 \delta(z - Vt) \quad (19)$$

and reduces (18) to

$$C_1^r(z, t) = (C_0/t) f_V(z/t) \quad (20)$$

where f_v is the pdf of the convection velocity. To select a specific stochastic-convection process, we assume that the velocities are lognormally distributed (Nielsen et al., 1973; Jury, 1985) with parameters μ_v and σ_v , and write (20) as

$$C_1^r(z,t) = \frac{C_0}{(2\pi)^{1/2} \sigma_\theta z} \exp \left(- \frac{(\ln z - (\mu_v + \ln t))^2}{2\sigma_\theta^2} \right). \quad (21)$$

To express the solute concentration as a function of cumulative infiltration I , we write the concentration in a single stream tube as

$$C_1^r(z, I; \vartheta) = C_0 \delta(z - I/\vartheta). \quad (22)$$

Inserting this in (18), the concentration of the lognormal stochastic-convection model as a function of space and cumulative infiltration may be written as

$$C_1^r(z, I) = \frac{C_0}{(2\pi)^{1/2} \sigma_\theta z} \exp \left(- \frac{(\ln z - (\ln I - \mu_\theta))^2}{2\sigma_\theta^2} \right). \quad (23)$$

where $\mu_\theta = \ln j_v$ and $\sigma_\theta = \sigma_v$ are obtained from the lognormal pdf of the velocities and (12).

Solute Spreading

The significant difference between a convection-dispersion process and a stochastic-convection process is the growth of the spread in the solute with time. We define the variance of the solute pulse by

$$\begin{aligned} \text{Var}(z) &:= \langle z^2 \rangle - \langle z \rangle^2 \\ &= \int_0^\infty z^2 f_z(z; I) dz - \left(\int_0^\infty z f_z(z; I) dz \right)^2, \end{aligned} \quad (24)$$

where $f_z(z; I) = C_I^f(z, I)/C_0$ is the pdf of the travel depth, i.e., the probability density for a tracer molecule to be at depth z after a cumulative amount of water I has infiltrated into the soil.

The first two depth moments of the convection-dispersion process may be calculated analytically by integrating over z in Laplace space and transforming the result back to normal space (Jury and Roth, 1990, Prob. 3.3). In the limit $I \gg \vartheta\lambda$, when the boundary does not influence the movement of the solute pulse any more, the variance of the convection-dispersion process may be written as

$$\text{Var}_{cd}(z) \approx 2\lambda(I/\vartheta) - 3\lambda^2 \quad I \gg \vartheta\lambda \quad (25)$$

and increases linearly with cumulative infiltration.

For a stochastic-convection process, the variance of the solute pulse is

$$\begin{aligned} \text{Var}_{sc}(z) = I^2 \bigg[& \int_0^{\infty} \vartheta^{-2} f_{\vartheta}(\vartheta) d\vartheta \\ & - \left(\int_0^{\infty} \vartheta^{-1} f_{\vartheta}(\vartheta) d\vartheta \right)^2 \bigg], \end{aligned} \quad (26)$$

which is obtained by inserting (22), divided by C_0 , and (18) into (24). As the expression in brackets is a constant that is determined by the pdf of the apparent water content, the variance increases quadratically with cumulative infiltration.

Preferential Flow

It is clear from the measured concentrations that the main pulse becomes depleted by preferential flow events. We do not attempt to describe the preferential flow process in detail, because it appears to depend in a highly non-linear way on a multitude of parameters and variables, like infiltration rate and prior water content. Instead, we account for the depletion of the main pulse by preferential flow in an average manner, by assuming that a constant fraction of the infiltration leads to preferential flow events and

that each event removes a constant fraction of the mass from the main pulse. This assumption leads to an exponential decrease of the total mass in the main pulse, yielding

$$C_1^r(z, l) = C_0 \exp\left(-\frac{l}{l_0}\right) \left[\left(\frac{\vartheta}{\pi \lambda l}\right)^{1/2} \exp\left(-\frac{(l - \vartheta z)^2}{4 \vartheta \lambda l}\right) - \frac{1}{2 \lambda} \exp\left(\frac{z}{\lambda}\right) \operatorname{erfc}\left(\frac{l + \vartheta z}{2(\vartheta \lambda l)^{1/2}}\right) \right] \quad (27)$$

for the convection-dispersion process (17), and

$$C_1^r(z, l) = \frac{C_0}{(2\pi)^{1/2} \sigma_\theta z} \exp\left(-\frac{l}{l_0}\right) \cdot \exp\left(-\frac{(\ln z - (\ln l - \mu_\theta))^2}{2\sigma_\theta^2}\right), \quad (28)$$

for the stochastic-convection process (23), where l_0 is the decay parameter.

Parameter Estimation

The parameters of the convection-dispersion model (27) and of the lognormal stochastic-convection model (28) were determined by fitting the models to the measured concentrations using the method of least squares. By our simplifying approximation (1), the model parameters $(C_0, \vartheta, \lambda, l_0)$ and $(C_0, \mu_\theta, \sigma_\theta, l_0)$, respectively, are constant.

To quantify the deviation of the model from the data, we first define the "distance" between the model $C_1^r(z, l; C_0, p_1, p_2, l_0)$ and the concentration $c(x, z, l)$ measured at horizontal position x and depth z after the infiltration l as

$$d(x, z, l; C_0, p_1, p_2, l_0) := \frac{c(x, z, l) - C_1^r(z, l; C_0, p_1, p_2, l_0)}{\sigma(x, z, l)}, \quad (29)$$

where $\sigma(x,z,l)$ is the standard deviation of the measured concentration and $(p_1, p_2) = (\vartheta, \lambda)$ for the convection-dispersion and $p_1, p_2 = (\mu_\vartheta, \sigma_\vartheta)$ for the stochastic-convection process. The deviation of the model from the data is then defined as the sum of the squared "distances" over all data points,

$$D^2(C_0, p_1, p_2, l_0) := \sum_{(x,z,l)} [d(x,z,l; C_0, p_1, p_2, l_0)]^2. \quad (30)$$

The model parameters are now determined by minimizing $D^2(C_0, p_1, p_2, l_0)$ using the Levenberg-Marquardt algorithm (Press et al., 1986). Figure 11 shows a comparison between the horizontally averaged measured concentrations, and the convection-dispersion and lognormal stochastic-convection model using the parameters given in Table 2.

If $c(x,z,l)$ is a realization of a random variable that is normally distributed with mean $C_l(z, l; C_0, p_1, p_2, l_0)$ and variance $\sigma^2(x,z,l)$ the D^2 is a χ^2 -distributed random variable. However, since we do not have any information about $\sigma(x,z,l)$, we consider it merely as a relative weighting factor and arbitrarily define it to be the same for all data points. After this definition, we clearly cannot assume that D^2 is χ^2 -distributed, and therefore cannot assess the validity of the model by a χ^2 -test.

Discussion

Preferential Flow. This experiment shows that a single uniform solute pulse applied to the surface of a natural soil may split into many pulses of varying velocities. The fast pulses, often referred to as preferential flow, can carry a fraction of the applied chemical well below the biologically active zone in a very short time. It appears that a fast pulse starts with every infiltration event whose intensity exceeds a certain threshold. The following picture offers a possible qualitative explanation of this phenomenon: We assume that the pore space may be divided into a matrix, typically consisting of small pores, and a macrostructure. For small infiltration rates, the matrix is not saturated and the transport characteristics of the soil depend only weakly on the infiltration rate. When

the infiltration rate exceeds a certain threshold, which depends on the antecedent water content, the matrix becomes saturated at some point in the profile, and water starts moving through the macrostructure, creating a preferential flow event. Initially, this preferential flow will flush the solutes from the matrix near the macrostructures, and eventually will decreasing the concentration to a level that is sustained by diffusion from the internal parts of the matrix. After flow in the macropores has stopped, concentrations in their immediate neighborhood increase again due to diffusive processes within the matrix. This sequence is repeated with every preferential flow event and slowly depletes the tracer mass in the slow velocity region without affecting its velocity. Actually, with the same infiltration rate, solute velocities in the slow velocity region will be lower with preferential flow than without, because only a fraction of the infiltrating water contributes to solute transport.

At the temporal and spatial resolution of this experiment, preferential flow appears as an extremely sporadic phenomenon. We did not attempt to analyse it in detail. Instead, we accounted for its effect on the main pulse in an average manner by assuming that it withdraws mass from the bulk in the matrix in an exponential manner. This approximation yields a satisfactory result, as far as the mass balance of the slow pulse is concerned, because preferential flow events are frequent in this experiment, but the effect of a single event on the main pulse is small. The same reasoning could not be applied to the preferential flow events themselves, however, because we might expect that each event would carry different tracer masses at different velocities and over different time intervals, depending in a complicated way on a multitude of conditions.

Process Model. Based on a comparison of modeled concentrations and horizontally averaged measured concentrations (Figure 11), we conclude that the convection-dispersion process is a more appropriate description of the main tracer pulse than the lognormal stochastic-convection process. The difficulty in assuming an *a priori* process model for solute transport on the field scale is demonstrated by comparing our conclusion with that of Butters and Jury (1989). They did a similar experiment in the morphologically homogeneous Etiwanda loamy sand under quasi-steady-state conditions

and found that the lognormal stochastic-convection model, calibrated at a depth of 0.3 m, yielded very good predictions for the observed area-averaged breakthrough curves down to depths of 1.8 m. Thus we deduce, that contrary to the morphological appearance, the Bülach soil is homogeneous on the transport scale, whereas the Etiwanda soil is not. We attribute this to the different typical thickness of soil layers, which is on the order of 0.1~m in the Bülach soil and an order of magnitude larger in the Etiwanda soil. Morphological layers in unsaturated soils often lead to interfaces for the solute transport that are perpendicular to the direction of the main solute flux. These interfaces may homogenize the transport characteristics of a soil either by increasing the transverse components of the solute flux, thereby mixing solutes that have travelled through different regions, or by interrupting longitudinal correlation structures in the transport volume.

TRANSFER FUNCTION MODELING OF SOLUTE ADSORPTION

In this study, a unified linear theory was developed for the transport of adsorbing solutes through soil. In this model the transport characteristics of the soil are expressed in terms of the travel time distribution of the mobile phase which is then used to incorporate local interaction processes. This approach permits the analysis of all linear transport processes, not only the small subset for which a differential description is known. From a practical point of view, it allows the direct use of measured concentrations or fluxes of conservative solute to characterize the mobile phase without first subjecting it to any model. This study is viewed as a vital step in the development of field-scale rate processes where adsorption modeling may have to be carried out in conjunction with experimental measurements of the transport properties in soils for which the transport description is not known *a priori*.

Analysis

We consider steady-state water flow through a soil that contains N types of adsorption sites. The dynamics of solute movement is described by equations for the conservation of mass in the mobile phase and in the adsorbed phases, and by an

equation for the flow in the mobile phase. To obtain the equations of mass conservation, we assume that (i) all phases are locally well-mixed, (ii) in equilibrium, the concentration ratio between any two given phases is independent of the concentrations, and (iii) the deviations from equilibrium are so small that nonlinear effects may be neglected. Then the mass transfer between any two phases may be described by a bilinear function of the concentrations in the two phases. To simplify the notation, we assume that the mass transfer from one adsorbed phase to another may be neglected.

The conservation of mass in the mobile phase may then be written as

$$\frac{\partial C_m^r}{\partial t} + J_m \frac{\partial C^f}{\partial z} = -\gamma_m \theta C_m^r - \sum_{i=1}^N \vartheta_i \beta_i (K_i C_m^r - C_i^r), \quad (31)$$

where C_m^r and C_i^r are the resident concentrations in the mobile phase and in the adsorbed phase i , respectively, C^f is the flux concentration, J_m the flux of the mobile phase, θ the volume fraction of the mobile phase, γ_m the decay rate in the mobile phase, γ_i the volumetric phase density of the adsorbed phase i , β_i the specific rate parameter for mass transfer from the mobile to the adsorbed phases, κ_i the distribution parameter for mass transfer between the mobile phase and the adsorbed phase i . The equation for the conservation of mass in the adsorbed phase i may be formulated as

$$\vartheta_i \frac{\partial C_i^r}{\partial t} = -\gamma_i \vartheta_i C_i^r + \gamma_i \beta_i (\kappa_i C_m^r - C_i^r), \quad i \in \{1, \dots, N\}, \quad (32)$$

where γ_i is the decay rate of the solute in phase i .

In its most general form, the equation describing the transport of a stable, non-adsorbing solute with the mobile phase relates the flux concentration to the resident concentration in the mobile phase, and may be written as

$$C^f = F [C_m^r] \quad (33)$$

where F is a linear operator on the space coordinate. For the convection-dispersion process, (33) may be written as (Kreft and Zuber, 1978):

$$C_{cd}^f = C_m^r - \frac{D}{V} \frac{\partial C_m^r}{\partial z}, \quad (34)$$

where D is the dispersion coefficient and V the pore velocity of the mobile phase.

The general solution of the linear system (31)-(33) for a flux boundary condition may be expressed in terms of its impulse response or transfer function, which is obtained by solving the system for the initial conditions

$$C_m^r(z,0) = 0, \quad C_i^r(z,0) = 0, \quad (35)$$

and the boundary conditions,

$$C^f(0,t) = \delta(t); \quad \lim_{z \rightarrow \infty} C^f(z,t) = 0, \quad (36)$$

where, for simplicity, we have assumed a semi-infinite soil.

$$\hat{C}^f = F [\hat{C}_m^r], \quad (37)$$

$$\hat{C}^f(0,t) = 1; \quad \lim_{z \rightarrow \infty} \hat{C}^f(z,t) = 0. \quad (38)$$

With some algebraic manipulations, we obtain

$$g(s)\theta \hat{C}_m^r + J_m \frac{\partial \hat{C}^f}{\partial z} = 0, \quad (39)$$

where

$$g(s) := s + \gamma_m + \sum_i \left(\frac{\vartheta_i \beta_i \kappa_i}{\theta} - \frac{\vartheta_i \beta_i^2 \kappa_i}{\theta(s + \gamma_i + \beta_i)} \right). \quad (40)$$

Using (37), we may write (39) in terms of the mobile resident concentration

$$g(s)\theta\hat{C}_m^r + J_m \frac{\partial F [\hat{C}_m^r]}{\partial z} = 0, \quad (41)$$

or, alternatively, apply the linear operator F to (39), thereby obtaining

$$g(s)\theta\hat{C}^f + J_m \frac{\partial F [\hat{C}^f]}{\partial z} = 0, \quad (42)$$

for the flux concentration. Here, we have used the fact that F operates only on the space coordinate and that the linear operators F and $\partial/\partial z$ commute. Comparing these two equations shows that the resident concentration in the mobile phase and the flux concentration obey the same equation. As we chose to formulate the boundary conditions in terms of the flux concentration, we will in the following only consider (42).

To solve (42), we need to know the process representation defining transport through the mobile phase. Instead of assuming an explicit form of the operator F , we assume that the dynamics are given implicitly by the probability density function (pdf) of the travel times in the mobile phase (Villermux, 1987). This pdf, which we denote by $f_m^f(z,t)$, contains all the information about the dynamics of solutes in the mobile phase and is equivalent to a description by a differential equation, if the latter exists. It may be regarded as the solution of (31) for a stable, non-decaying solute ($\gamma_m = 0$; $\gamma_i = 0$, $\forall_i$) for the initial and boundary conditions given by (35) and (36). For this case, (40) becomes

$$g(s) = s, \quad (43)$$

and (42) simplifies to

$$s\theta\hat{C}^f + J_m \frac{\partial F [\hat{C}^f]}{\partial z} = 0. \quad (44)$$

Comparing (44) and (42), and noting that $g(s)$ is not a function of the space variable z , we see that the solution $\hat{f}^f(z;s)$ of (42) may be written in terms of the solution $\hat{f}_m^f(z;s)$ of (44) as

$$\hat{f}^f(z;s) = \hat{f}_m^f(z;g(s)). \quad (45)$$

In general, $f_m^f(z,t)$ is directly measurable, e.g., as the result of a bromide-tracer experiment.

Example: Single Adsorption Site

We consider a soil that has only a single type of adsorption sites characterized by the volumetric phase density ϑ , the specific rate parameter β and the distribution coefficient κ . The solute may decay in the mobile phase and in the adsorbed phase through a first order reaction with rates ϑ_m and ϑ , respectively.

The solution to this system for the case of one adsorption site is derived in Roth and Jury (1992). In terms of the travel time pdf, $f_m^f(z,t)$, of a mobile, non-adsorbing tracer (which may be represented by a process model if known, or by nonparametric data), the travel time $f(z,t)$ of the sorbing tracer is given by

$$f^f(z,t) = f_m^f(z,t) \exp(-at) + \int_0^t f_m^f(z,\tau) \exp(-a\tau) \mathfrak{R}(t-\tau, b\tau, c) d\tau, \quad (46)$$

where

$$\mathfrak{R}(t,b,c) := \sqrt{(b/t)} \exp(-ct) I_1(2\sqrt{bt}) \quad (47)$$

and I_1 is the modified Bessel function of order 1. The integral in (46) will in general have to be evaluated numerically. This result, although restricted to a convection-dispersion

process, was already obtained by Lassey (1988) by adapting a solution of Hubert et al. (1971) and was later used by Cvetkovic and Shapiro (1990) with a piston flow process.

To illustrate some typical flux pdfs, we consider in the following a semi-infinite soil with a steady water flux. Solute movement in the water phase is assumed to be a convection-dispersion process which we describe as a function of cumulative infiltration $I := J_m t = Vt/\theta$ pesticide by

$$f_m^f(z, I) = \sqrt{\frac{\theta z^2}{4\pi\lambda I^3}} \exp\left(-\frac{(I-\theta z)^2}{4\theta\lambda I}\right), \quad (48)$$

where $\lambda := D/V$ is the dispersivity. To get a simpler expression, we introduce the dimensionless infiltration $I' := I/(I_m)$, where $(I_m) = \theta z$ is the expectation value for the amount of infiltration it takes to move a non-adsorbing solute particle from the surface to the depth z , and write (48) in dimensionless form as

$$f_m^f(I') = \sqrt{\frac{Pe}{4\pi I'^3}} \exp\left(-\frac{(I'-1)^2}{4I'/Pe}\right), \quad (49)$$

where $Pe := z/\lambda$ is the Peclet number.

Adsorption is assumed to be the rate-limited process. Substituting the Laplace transform of (49),

$$\hat{f}_m^f(s) = \exp\left(-\frac{Pe}{2} (1 - \sqrt{1 + 4s/Pe})\right), \quad (50)$$

into (45) yields the flux pdf of the adsorbing solute in Laplace space, $\hat{f}^f(s)$, which is inverted most conveniently with the Talbor algorithm.

Data Set

In this section, we apply the theory to analyze a set of data from a laboratory experiment described by Elabd (1984). For this experiment 40 soil columns (36

undisturbed, 4 repacked) with a diameter of 100 mm and a length of 150 mm were taken from a loamy sand field in Etiwanda, CA. In the laboratory, steady state solute flow of an 8 meq L⁻¹ CaSO₄ irrigation solution at an average flow rate of 40 mm d⁻¹ was established in each of the columns. The solution was dripped through a pinhole onto the top center of each column and the freely draining solute was collected in narrow-neck bottles. After steady state was reached, a pulse of CaCl₂ (8 meq L⁻¹) and napropamide (50 mg L⁻¹) was applied with 5 mm of irrigation water. During the entire experiment no ponding was detected on any column. Initially, the drainage water was sampled every 4 hours. After the chloride concentrations had reached the detection limit, the sampling interval was increased to one day. A more complete description of the experiment is given by Elabd (1984) and Jury et al. (1986a).

During the experiment solute concentrations were measured in the effluent from a certain time interval and recorded together with the total amount of effluent since the application of the solute pulse. A measured concentration C_i thus represents an integrated value over the corresponding amount of effluent $\Delta I_i = I_i - I_{i-1}$ for the interval i . To prevent systematic errors, we estimate the flux pdf as a function of infiltration at the midpoint of each interval as

$$f^*((I_i + I_{i+1})/2) = \frac{C_i}{\sum_{j=1}^N C_j \Delta I_j}, \quad i=1, \dots, N. \quad (51)$$

Our basic hypothesis for the following analysis is that the measured napropamide concentrations can be modeled as a rate-limited adsorption process superimposed on a transport process whose characteristics can be estimated independently from the measured chloride concentrations. Due to the short duration of the experiments, decay will be neglected in both phases. It is clear from the setup of the experiment that the flow field in the columns is rather complicated. The solute enters at the center of the column top and spreads into a three-dimensional structure during the transport. We do not know *a priori* if the asymptotic limit that would allow the convection-dispersion assumption is reached over the short length of the column. Furthermore, the water content in the columns is not constant, because the free drainage creates a nearly saturated lower

boundary region. As an illustration of the ways in which the theory can be used, we will analyze the napropamide data twice, first assuming that Cl^- obeys the CDE, and second by using the data alone without modeling the transport process explicitly.

Fitted pdfs

Some typical examples of measured and fitted pdfs are shown in Figure 12, where the solid line represents the CDE simulation and the dots the data representation for Cl^- . The first row shows a poorly resolved pdf for the chloride, which seems to be described adequately by the data simulation with a low water content $\theta = 0.20$ and a large dispersivity $\lambda = 25.7$ mm. However, the napropamide data reveal that the peak probably consists of a superposition of two peaks. Both models overestimate the spreading of the napropamide, and the data simulation actually indicates that only the part of the napropamide that corresponds to the fast pulse has been measured.

The pdfs shown in the second row also indicate the presence of two peaks. However, while the peaks postulated for the first row were of comparable size, the first peak is now much smaller and the resolution of the second one is sufficient. Due to its structure, the CDE model of Cl^- cannot capture the early arrival of chloride and consequently the approach fails to model the early part of the napropamide pdf. In contrast, the adsorbing model using the measured chloride pdf directly describes the measured napropamide pdf much better.

The pdfs of the third row may be interpreted as a superposition of three peaks, where the small first peak and the main peak are almost merged. Again, the data representation describes the measured napropamide pdf rather well, whereas the CDE representation misses the first peak. We do not know whether the third peak visible in the chloride pdf would eventually have showed up in the napropamide pdf as the measurements had been stopped too early.

A superposition of a number of poorly resolved similar peaks may be guessed from the chloride pdf shown in the fourth row. Both models yield similar values for the retardation coefficient, 11.0 and 11.5, respectively, but only the data representation produces the correct shape of the pdf.

While some of the measured pdfs offer clear evidence of multiple peaks, the majority consists of slightly deformed single peaks as the example shown in the last row. Some of the solute typically arrives earlier than describable by a convection-dispersion process and there is often some tailing. Although the chloride pdf thus cannot be modeled by the data representation, the napropamide pdf may be described equally well by either model due to the additional spreading caused by a small rate parameter β .

Although the main features of the napropamide pdf are generally well described by the data model, a much higher resolution of the chloride pdf would be required to capture its details. It follows that as a general rule, the pdf of the conservative solute should be higher resolved than that of the adsorbing solute by a factor R , where R is the retardation factor. In practice this is easily accomplished because the analysis of the conservative solute is generally very much faster than that of the adsorbing solute.

SPATIAL VARIABILITY OF WATER AND SOLUTE FLUX

Although significant information has now been gained about the spatial distribution or spatial correlation scale of transport properties, water and solute flux has seldom, if ever, measured on a comparable resolution. Since the spatial distribution of the fluxes will ultimately be required for any theoretical advances in the area of equilibrium and rate-limited mass-exchange processes, we designed and conducted a field study at the Etiwanda site to address this question.

The primary purpose of the study was to investigate the effects of cultivation and irrigation method on uniformity of water flow and diversion of solutes leached under field conditions. Outflow from an undisturbed, unsaturated field soil contained in a 0.8 m x 0.8 m x 0.3 m deep lysimeter was sampled by a 64-cell grid of fiberglass wick solution samplers, whose performance was described in Poletika et al. (1992). Daily 20-mm water inputs were applied at a rate of 5 mm per hour by hydraulic nozzles mounted on a motorized boomer by low-volume sprinklers. Narrow pulse inputs of chloride, nitrate and bromide solutions were used to evaluate solute dispersion and travel paths. Detailed results of this study and its conclusions are given in Poletika and Jury (1992).

The full field study tested a number of separate aspects of the spatial variability of water and chemical movement. The principal findings of relevance to the rate process characterization were:

- 1) Chemical and water appeared to redistribute into zones of nonuniform flux at a region very near the soil surface. After that, downward movement proceeded relatively one-dimensionally. For such a system, parallel stream tubes would characterize the flow extremely well, provided that water and solute redistributed prior to the development of the stream tube model, or that transfer functions were used directly to characterize the solute travel time distribution.
- 2) Despite nearly 100% spatial uniformity of the water input distribution, there was substantial spatial variation in water and solute flux at the 36 cm depth, with a coefficient of variation of water flux of 53% and a range from 12.5 to 462.5 mm collected during single sample intervals among the 64 locations. The rank order of water flux did not change over time, with the highest and lowest locations persisting through a series of irrigations.
- 3) A small rearrangement of the surface few mm resulted in a dramatic decrease in solute dispersion for the area-averaged pulse recovered at 30 cm. This result, together with the histogram giving the distribution of water flow at individual collectors, is shown in Fig. 13.

ANALYSIS OF FIELD METHODS USED TO MEASURE HYDRAULIC CONDUCTIVITY

As stochastic methods are developed for the determination of transport problems in unsaturated soil, new questions arise about the relationship between the spatial scale of the measurement device and the spatial scale of the simulation. In addition, questions arise about the consistency of the different methods proposed for measurement of key properties. In a study designed to coordinate the modeling efforts of the Israeli and US groups, the Riverside investigators used the stochastic modeling approach of Russo in 1991 to represent the water flow and hydraulic property variability of a typical heterogeneous field. The purpose of the study was to utilize specific field-oriented methodologies for determining the hydraulic conductivity as a function of water content

or matric potential, and to compare the results obtained by different methods to the true underlying variability imposed in the numerical representation of the hydraulic property distribution.

Complete results are given in Tseng and Jury (1992). The principal methodologies and results are briefly sketched below.

Following the method utilized by Russo (1991) and Russo and Dagan (1991), we developed a two-dimensional representation of flow using the Richards flow equation together with the assumption that the field obeyed geometric similitude scaling theory, with a scaling factor distribution that was second-order stationary and possessing a correlation structure that was much longer in the horizontal than in the vertical direction. All methods analyzed utilized data obtained from the most common method of measuring hydraulic conductivity in the field, that of a redistribution experiment monitored by tensiometers and neutron probes or TDR probes to determine matric potential and hydraulic conductivity as a function of time during redistribution. A review of many field methods is given in the paper by Libardi et al. (1980). Three different types of parameter estimation were used in the study: 1) analyses of effective hydraulic conductivity assuming that the field drained by gravity flow, 2) analyses of hydraulic conductivity and matric potential patterns on the assumption that the Richards flow equation is valid in one dimension, and 3) analyses of hydraulic conductivity patterns using the method of predicting hydraulic conductivity from matric potential proposed by Mualem and developed by van Genuchten. Results of the comparisons among models are given in Figure 14.

In general, the methods based on gravity flow gave very poor estimates of the true underlying soil properties. This is particularly disturbing given that this is the most common method for field evaluation of the properties (Libardi et al., 1980). The direct method using the inversion of the Richards flow equation was accurate only if the tensiometer distribution and the water content distribution measurements were taken very close to each other and replicated laterally. Finally, the van Genuchten method was sometimes accurate and sometimes not, depending on the spatial relationship between the water content and tensiometer measurements. The full impact of the van Genuchten

model was not assessed, since the hydraulic properties were estimated on the assumption that the model used by Mualem is valid. Therefore, part of the uncertainty of the estimate due to this being a poor model assumption was not assessed in this study.

OVERALL EVALUATION AND SIGNIFICANCE OF RESULTS

Because this study worked with a variety of field data sets at its foundation, we were able to evaluate theoretical approaches to unsaturated zone flow and transport under widely differing conditions. Such a perspective is valuable because each field we examined contained unique elements that required site-specific approaches. Consequently, one of the major contributions that can be stressed from our study is that it is very unlikely that universal model approaches can be developed to describe simulation on all soils. Rather, certain unique characteristics of individual soils must be recognized and classified, and specific models developed for these particular categories. The groundwork for developing such a categorization has been laid in this study.

The significance of the findings in this study can be organized into five different sections: 1) feasibility of stochastic continuum modeling, 2) implications of preferential flow and soil layering on transport, 3) mixing processes and spatial variability of flow in alluvial soils, 4) characterization and modeling of adsorption rate processes, and 5) interpretation of field methods for hydraulic property measurements. These are discussed individually below.

1. Stochastic Modeling of the Unsaturated Zone

This comprehensive study centered in Israel has made major progress toward implementing a theory that is widely accepted in groundwater flow to the more complex regime of unsaturated flow where the model assumptions are less certain. The main conclusions drawn by the Israeli research study are as follows.

- 1) Existing, simplified stochastic vadose zone transport models that treat the soil as though it were composed of a series of isolated, vertical stream tubes with different

velocities [represented by the models of Dagan and Bresler (1979) and Jury (1982)] may describe the solute spread at shallow depths near the solute entry zone ("near-field"), but may fail to describe the spread of a solute plume at larger depths ("far-field"), mainly because of the neglect of vertical heterogeneity in the soil hydraulic properties.

- 2) The stochastic model developed in this research project (Russo, 1992) for the transport of the ensemble-average concentration of a tracer solute in a heterogeneous, partially-saturated porous formation that takes into account the multi-dimensionality of variations in the hydraulic properties can describe "far-field" solute spread, which in turn approaches an asymptotic Fickian behavior after the solute body has travelled a sufficient distance (i.e., a few tens of conductivity correlation scales). Results obtained by using this stochastic transport model are consistent with results obtained by the theory of transport by groundwater flow (e.g., Dagan, 1984).
- 3) Results of the transport simulation conducted in this research project (Russo, 1991) and its accompanying analysis (Russo and Dagan, 1991), as well as the results of the stochastic model (Russo, 1992), suggest that despite the complexity of unsaturated flow as compared with saturated flow under certain circumstances (i.e., gravitational flow), vadose zone transport might be amenable to a similar analysis as saturated groundwater transport. Because of the complexity of unsaturated flow as compared with saturated flow, however, in unsaturated flow the necessary input data for the analysis should include statistical parameters of both formation properties - $\log K_s$ and α , as well as mean values of the response variables - water saturation or capillary pressure head. Based on our analysis (Russo, 1992), it may be concluded that the earlier finding (Russo and Dagan, 1991) regarding the relative robustness of the product of the conductivity variance and its correlation scale to water saturation may be considered a valid, general result, as long as the correlation scale of α is relatively small compared with the correlation scale of $\log K_s$.

- 4) There is an immediate need for additional field studies to characterize the spatial variability in soil properties relevant to vadose zone transport, and for field-scale, controlled, transport experiments to further validate existing stochastic transport models. Inasmuch as stochastic models of solute transport predict the ensemble-average spread of a solute body, while field experiments provide information on the spread of a single solute body for particular, site-specific applications (i.e., a single realization from an ensemble of many plausible realizations), care should be taken in the design of transport experiments. For purposes of model validation, the design problem can be formulated with the objective of reducing uncertainties about the ensemble-average solute flux and accumulated mass at a given control plane. Inasmuch as these uncertainties decrease with the ratio of the size of the solute inlet zone to the size of the correlation scales of the relevant soil properties normal to the mean flow direction, the required size of the solute inlet zone in the transport experiment can be evaluated from the correlation scale of the log-unsaturated conductivity, using the Lagrangian framework developed by Dagan et al. (1992).

Finally, the results of the stochastic models addressed in this research project together with additional field data of soil properties relevant to vadose-zone solute transport, as well as data from field-scale transport experiments, may improve our understanding of field-scale solute spread in partially-saturated soils, and may serve for the subsequent development of field-scale transport models for complex, real-world scenarios.

2. Transport in Layered Soil Under Conditions of Preferential Flow

The Bülach field manifested a type of spatial variability that lies outside of the assumptions of existing models for transport at the local scale. In particular, the finding that approximately half of all chemical movement occurred through preferential flow channels in the top several m of soil represents an extreme not found in prior field studies. In addition, the strong layering caused lateral mixing to occur within the soil matrix that actually favored the convection dispersion model over a stochastic convective process that would be expected to dominate in alluvial soils. Finally, the decoupling of

the fast and slow zones allowed each region to be represented separately, a modeling simplification that may provide valuable insight into future studies on fields of this nature. This field clearly represents an extreme of the type for which we had no experimental information, and therefore developed no theoretical insight. As a result of the study, soils of this type will now be researched more extensively in the future and their implications studied thoroughly.

3. Spatial Variability of Transport in Alluvial Soils

The Etiwanda field soil is one which has been researched more extensively than perhaps any other unsaturated zone in the United States. In previous studies (Butters et al., 1991; Jury et al., 1986; Ellsworth et al., 1991; Ghodrati and Jury, 1992), the field showed almost pure stochastic convective flow to a depth of 3 m and showed solute adsorption behavior which was not consistent with equilibrium adsorption. The study reported herein was designed to quantify the small-scale spatial variability on this field and to determine to the degree possible the mechanisms responsible for spatial variability. The major conclusions drawn from the study were that the solute and water mixing processes occurred very near the surface and continued downward thereafter with essentially no lateral mixing. This is in direct contrast to the behavior in the Bulach field and indicates, as pointed out by the Israeli researchers, that in the shallow zone isolated stream tube models may perform extremely well provided that lateral mixing does not occur to any extent.

4. Characterization of Rate Processes

The major conclusion drawn by this study is that solute adsorption can be isolated from transport and studied independently through the use of dual tracers. For soils showing any pronounced deviation from convective-dispersive flow, this represents a means whereby the rate processes may be characterized through the use of dual tracers without having to simultaneously evaluate transport parameters in a complex medium. The superior performance of the nonparametric method of flow characterization to that first fitting the convection-dispersion equation demonstrated in this study illustrates the

potential for improved identification of solute rate parameters in heterogeneous soil. This improved identification would be the first step toward extending characterization of flow and transport to sorbing solutes, which would substantially advance the predictive modeling of hazardous contaminants.

5. New Field Methodologies for Measurement

The major conclusions drawn by this stage of the study indicate that currently used methods for evaluating hydraulic properties may have substantial limitations when applied to heterogeneous field soil. The fact that the most commonly used methods performed poorest indicates that calibration procedures for models may have to be conducted using yet-untried methodologies in order to develop realistic representations of the transport property variability.

COOPERATION BETWEEN INVESTIGATORS

Although the specific projects executed in Israel and the United States were distinct, the methodology, philosophy and objectives were coordinated. The stochastic modeling endeavor conducted in Israel was designed to make use of the substantial expertise at that institution in stochastic continuum modeling. To coordinate the findings and methodologies at that institution, a transport model utilizing the same structural hypotheses was developed at Riverside and used to address a companion project that would be compatible with the Israeli one.

At UC Riverside, the investigators focused largely on transfer function modeling and experimentation conducted in Riverside and Switzerland while the senior author was on sabbatical. This approach, however, largely involves the so-called stochastic stream tube hypothesis which is one of the asymptotic limits employed by the Israeli workers in their analysis of transport through heterogeneous unsaturated zones. Finally, the experimental information utilized in Israel was generated partly through their own field

study and partly through analysis of Riverside data sets involving the work of Butters, Ellsworth and Roth/Schulin.

As a result, even though the modeling exercises were conducted in parallel, they were coordinated and used to cover compatible areas of inquiry. The resulting information base is therefore applicable to either region and as well has extended the dominion of field-scale solute transport modeling far beyond the point where it was when the project initiated.

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1. Poletika N, Jury WA (1992) Effect of soil surface management on water flow distribution and solute dispersion. *Soil Sci Soc Amer J* (submitted in August 1992).
2. Russo D (1991) Stochastic analysis of vadose-zone solute transport in a vertical cross-section of heterogeneous soil during nonsteady water flow. *Water Resour Res* 27:267-283.
3. Russo D (1992) Stochastic modeling of macrodispersion for solute transport in a heterogeneous unsaturated porous formation. Submitted to *Water Resour Res*.
4. Russo D, Dagan G (1991) On solute transport in a heterogeneous porous formation under saturated and unsaturated flows. *Water Resour Res* 27:285-293.
5. Roth K, Jury WA, Flühler H, Attinger W (1991) Transport of chloride through an unsaturated field soil. *Water Resour Res* 27:2533-2541.
6. Roth K, Jury WA (1992) Linear transport models for homogeneous soils. *Water Resour Res* (submitted in December 1991).
7. Tseng P, Jury WA (1992) Simulation of field measurement of hydraulic properties in heterogeneous field soil. *Water Resour Res* (submitted in August 1992).

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Table 1. Water and solute field data sets used in this study.

Field	Size	Measurements	Reference
<u>Water Flow</u>			
Etiwanda [†]	0.64 ha	70 permeameter measurements of $K(\theta)$, $h(\theta)$	Jury et al., 1990
Bet Dagan [†]	20 m transect to 2.5 m	417 cores characterizing spatial structure of K_s , α	Russo and Bouton, 1992
<u>Solute Transport</u>			
Etiwanda	0.64 ha	36 undisturbed soil columns used for Cl^- , pesticide leaching	Jury et al., 1986
Etiwanda	0.64 ha	102 solution samplers measuring Br^- pulse leaching	Butters et al., 1989
Etiwanda	0.64 ha	14 Cl^- massive plume leaching studies	Ellsworth et al., 1991
Bülach [‡]	10 m transect	Cl^- leaching monitored by 110 solution samplers	Roth et al., 1991
Creux de Chippio [§]	15 m transect to 3 m	Br^- and Cl^- leaching monitored by 79 soil cores	Shulin et al., 1987
Etiwanda	1 m ² plot	Br^- , pesticide leaching monitored by 64 drainage collectors 10 x 10 cm ²	Poletika and Jury, 1992

[†]structureless loamy sand

[‡]structured, layered silt loam/silty clay loam

[§]stoney sandy loam

Table 2. Model parameters of the convection-dispersion and the lognormal stochastic-convection model.

Convection-Dispersion		Stochastic-Conversion	
Parameter	Value	Parameter	Value
C_0	17.7 mol m ⁻²	C_0	22.9 mol m ⁻²
ϑ	1.45	μ_ϑ	-0.309
λ	0.29 m	σ_ϑ	0.834
l_0	0.995 m	l_0	0.955 m

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- Fig. 1a. Distribution of $\log K_s$ (K_s in cm/min) in the upper 2.5 m of the vertical cross-section at Bet Dagan site (from Russo and Bouton, 1992). Vertical exaggeration 2.1X.
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- Fig. 4b. Longitudinal vertical component of macrodispersivity tensor (bottom) λ_{11} , as a function of travel time, t . Values of $\lambda_{11}(t)$ evaluated from the first derivative of cubic splines fitted to the $X_{11}(t)$ data (Fig. 5a), are given by the dashed-dotted lines. Values of $\lambda_{11}(t)$, evaluated from the depth-moment integrals of the depth-scaled, one-dimensional vertical CDE, using the horizontally averaged values of concentration as a function of depth, are given by the dashed lines. The solid line is $\lambda_{11}(t)$, derived by Dagan (1984) for two-dimensional, steady, saturated flow.
- Fig. 5a. Longitudinal (X_{11}) component of the displacement covariance tensor estimated from the second spatial moment of the measured solute plume about its center of gravity at the Etiwanda site (from Ellsworth, 1989), as a function of travel time, t .
- Fig. 5b. Longitudinal vertical component of macrodispersivity tensor, λ_{11} , estimated from the second spatial moment of the measured solute plume about its center of gravity at the Etiwanda site (from Ellsworth, 1989), as a function of travel time, t .

FIGURES (continued)

- Fig. 6. Scaled longitudinal ($X'_{11} = X_{11}/l_{f1}^2 \sigma_f^2$) and transverse ($X'_{22} = X_{22}/l_{f1}^2 \sigma_f^2$) components of the displacement covariance tensor as a function of scaled travel time, $t' = tU_1/l_{f1}$, for different water saturations, S_e , denoted by the numbers labeling the curves (Russo, 1992). Dashed lines represent closed-form analytical expressions of $X'_{11}(t')$ and $X'_{22}(t')$ derived by Dagan (1984) for steady saturated flow in a three-dimensional, isotropic structure. U_1 is the mean velocity (vertical), σ_f^2 is log-saturated conductivity variance, CV_α is the coefficient of variation of α , l_{f1} and l_{a1} are the correlation scales in the vertical direction of log K_s and α , respectively, and $\rho = l_f/l_{f1} = l_a/l_{a1}$ is the aspect ratio.
- Fig. 7. Scaled longitudinal ($D'_{11} = X_{11}/2tU_1l_{f1}\sigma_f^2$) and transverse ($D'_{22} = X_{22}/2tU_1l_{f1}\sigma_f^2$) components of the apparent macrodispersivity coefficient, as a function of scaled travel time, t' , for different water saturations, S_e (denoted by the numbers labeling the curves). Dashed lines represent closed-form analytical expressions of $D'_{11}(t')$ and $D'_{22}(t')$, derived by Dagan (1984) for steady saturated flow in three-dimensional, isotropic structure. Values and symbols are as in Fig. 6.
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FIGURES (continued)

- Fig. 11. Comparison between horizontally averaged measured concentrations (same as in Fig. 8) and the best fitting convection-dispersion and log-normal stochastic-convection model. The cumulative infiltration is normalized by dividing by the estimated average volumetric water content $\theta = 0.34$. The shaded bar shows the depth to which data were used to estimate the model parameters. The rightmost frames show the absolute value of the difference between the respective model and the averaged data. (We did not use this difference to estimate the model parameters; all data points were used individually without prior averaging.)
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Fig. 1a

Fig. 2

Fig. 3

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Fig 14

1000-200000

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