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**Characterization of Field-Scale Transport in Spatially
Variable Unsaturated Field Soils**

W.A. Jury, D. Russo

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

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William A. Jury
Department of Soil and Environmental Sciences
University of California, Riverside, CA 92521, USA

David Russo
ARO Institute of Soils and Water
The Volcani Center, Bet Dagan, 50250, Israel

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Abstract

This report describes activity conducted in several lines of research associated with field-scale water and solute processes. A major effort was put forth developing a stochastic analysis of a macroscopically heterogeneous medium using the technique of stochastic continuum analysis for an important class of problems involving flow of reactive and nonreactive chemicals under steady unsaturated flow. The field-scale velocity covariance tensor has been derived from local soil properties and their variability, producing a large-scale description of the medium that embodies all of the local variability in a statistical sense. Special cases of anisotropic medium properties not aligned along the flow direction and of spatially variable solute sorption were analysed in detail, revealing a dependence of solute spreading on subtle features of the variability of the medium, such as cross-correlations between sorption and conductivity.

A novel method was developed and tested for measuring hydraulic conductivity at the scale of observation through the interpretation of a solute transport outflow curve as a stochastic-convective process. This undertaking provided a host of new $K(\theta)$ relationships for existing solute experiments and also laid the foundation for future work developing a self-consistent description of flow and transport under these conditions. Numerical codes were developed for calculating $K(\theta)$ functions for a variety of solute pulse outflow shapes, including lognormal, Fickian, Mobile-Immobile water, and bimodal. Testing of this new approach against conventional methodology was mixed, and agreed most closely when the assumptions of the new method were met. We conclude that this procedure offers a valuable alternative to conventional methods of measuring $K(\theta)$, particularly when the application of the method is at a scale (e.g. an agricultural field) that is large compared to the common scale at which conventional $K(\theta)$ devices operate. The same problem was approached from a numerical perspective, by studying the feasibility of inverting a solute outflow signal to yield the hydraulic parameters of the medium that housed the experiment. We found that the inverse problem was solvable under certain conditions, depending on the amount of noise in the signal and the degree of heterogeneity in the medium.

A realistic three dimensional model of transient water and solute movement in a heterogeneous medium that contains plant roots was developed and tested. The approach taken was to generate a single realization of this complex flow event, and examine the results to see whether features were present that might be overlooked in less sophisticated model efforts. One such feature revealed is transverse dispersion, which is a critically important component in the development of macrodispersion in the longitudinal direction. The lateral mixing that was observed greatly exceeded that predicted from simpler approaches, suggesting that at least part of the important physics of the mixing process is embedded in the complexity of three dimensional flow. Another important finding was the observation that variability can produce a pseudo-kinetic behavior for solute adsorption, even when the local models used are equilibrium.

Objectives of the Research Proposal

1. To develop new methods for quantifying spatial variability of local soil hydraulic properties, and for determining effective macroscopic hydraulic properties for field-scale unsaturated flow
2. To analyse field-scale solute transport under transient, unsaturated flow regimes that contain plant roots taking up water and also preferential flow paths
3. To test the applicability of existing stochastic models of vadose-zone field-scale transport to realistic flow and transport conditions

1. Stochastic Analysis of the Velocity Covariance and the Displacement Covariance Tensors in Partially Saturated Heterogeneous Porous Formations

1.1 Theoretical Considerations

1.1.1 First-Order Approximations of the Velocity Covariance Tensor

A heterogeneous porous formation with an anisotropic structure, under steady, unsaturated flow, in a Cartesian coordinate system (x_1, x_2, x_3) , with x_1 directed vertically downwards, is considered. The extent of the flow domain (as well as the length scale of the nonuniformity of the average flow) is much larger than the scales of the formation heterogeneity. It is assumed that at the core scale, (characterizing an elementary volume (REV), small compared with the scale of the formation heterogeneity, but containing many pores), the unsaturated flow obeys Darcy's law and continuity. Neglecting local anisotropy, the equation governing the steady-state unsaturated flow locally, can be written as:

$$\frac{\partial^2 \psi}{\partial x_i^2} + \frac{\partial \log K}{\partial x_1} + \frac{\partial \log K}{\partial x_i} \frac{\partial \psi}{\partial x_i} = 0 \quad (1.1)$$

where $\underline{x}=(x_1, x_2, x_3)$ is the coordinate of the centroid of the REV, $\psi=\psi(\underline{x})$ is capillary pressure head (considered here as a positive quantity), $K=K(\underline{x}, \psi)$ is unsaturated conductivity and $i=1, 2, 3$.

It is further assumed that the relations between K and ψ at the core scale are described by the expression of Gardner [1958]:

$$\log K(\psi, \underline{x}) = \log K_s(\underline{x}) - \alpha(\underline{x}) \psi(\underline{x}) \quad (1.2)$$

where $\log K_s$ is log-saturated conductivity and the parameter α is the reciprocal of the macroscopic capillary length scale, λ [Raats, 1976].

The parameters and the variables in (1.1) and (1.2) are expressed in terms of means and perturbations, i.e.,

$$\psi = H + h; \alpha = A + a; \log K_s = F + f; \log K = Y + y \quad (1.3a)$$

where

$$Y = F - AH - E[ah]; y = f - Ah - aH - ah \quad (1.3b)$$

Both formation properties, $\log K_s$ and α , are viewed as multivariate normal (MVN) RSFs, ergodic over the region of interest, characterized at second order by constant means, $F = E[\log K_s]$ and $A = E[\alpha]$, and by statistically-anisotropic, two-point covariance functions, $C_{ff}(\xi)$ and $C_{aa}(\xi)$, respectively, and cross-covariance function, $C_{fa}(\xi)$ given by:

$$C_{pp}(\xi) = \sigma_p^2 \exp(-\xi') \quad (1.4)$$

where $p=f, a$ or fa ; $\xi' = (\underline{x} - \underline{x}')/I_p$ is the scaled separation vector, $\xi' = |\xi'|$; σ_f^2 and σ_a^2 , and $I_f = (I_{f1}, I_{f2}, I_{f3})$ and $I_a = (I_{a1}, I_{a2}, I_{a3})$ are the respective variances and correlation scales of $\log K_s$ and α ; $\sigma_{fa}^2 = \rho_{fa} \sqrt{(\sigma_f^2 \sigma_a^2)}$ and ρ_{fa} are the cross-variance and the cross-correlation coefficient between perturbations of $\log K_s$ and α ; and $I_{fa} = 2I_f I_a / (I_f + I_a)$.

Eq. (1.2) implies that for a given mean capillary pressure head, $H(\Theta)$, where Θ is mean water saturation, log-unsaturated conductivity, being a linear combination of $\log K_s$ and α ,

is also MVN, and its probability density function (PDF) is characterized completely by the mean $Y(\Theta)=F-AH(\Theta)$ and the covariance, $C_{yy}(\xi;\Theta)$, given by:

$$C_{yy}(\xi;\Theta) = C_{ff}(\xi) + H^2(\Theta)C_{aa}(\xi) - 2H(\Theta)C_{fa}(\xi) \\ + A^2C_{hh}(\xi;\Theta) - 2AC_{fh}(\xi;\Theta) + 2AH(\Theta)C_{ah}(\xi;\Theta) \quad (1.5)$$

where $C_{hh}(\xi;\Theta)$ is the covariance function of the capillary pressure head perturbation, and $C_{fa}(\xi)$, $C_{fh}(\xi;\Theta)$ and $C_{ah}(\xi;\Theta)$ are the cross-covariance functions between perturbations of $\log K_s$ and α , $\log K_s$ and ψ , and α and ψ , respectively.

The mean steady-state unsaturated flow equation is obtained by substituting (1.3) in (1.1), neglecting the term $E[ah]$ in (1.3b) and taking expected values of both sides of the resultant [Yeh et al., 1985a], i.e.,

$$\frac{\partial^2 H}{\partial x_i^2} + \frac{\partial (F-AH)}{\partial x_1} + \frac{\partial (F-AH)}{\partial x_i} \frac{\partial H}{\partial x_i} + \left\langle \frac{\partial (f-Ah-aH-ah)}{\partial x_i} \frac{\partial h}{\partial x_i} \right\rangle = 0 \quad (1.6a)$$

Subtracting (1.6a) from (1.1), neglecting products of perturbations, the linearized steady-state unsaturated flow perturbation equation [Yeh et al., 1985a] is:

$$\frac{\partial^2 h}{\partial x_i^2} - A(2J_i - \delta_{1i}) \frac{\partial h}{\partial x_1} - J_i(J_i - \delta_{1i})a + J_i \left(\frac{\partial f}{\partial x_i} - H \frac{\partial a}{\partial x_i} \right) = 0 \quad (1.6b)$$

where $\mathbf{J}=(J_1, J_2, J_3)$ is the mean head gradient vector and δ_{1i} is the Kronecker delta.

For saturated flow, capillary pressure, and, concurrently, the parameter α , which determines the rate of decrease of $\log K$ with ψ , are irrelevant. Eliminating α from Eqs. (1.6a) and (1.6b), they are reduced to the steady-state mean saturated flow equation and the

linearized saturated flow perturbation equation, respectively, (e.g., Bakr et al. [1978]).

Representing (1.6b) by the stochastic Fourier transform integral, the first-order approximation for the relationship among the Fourier amplitudes of the perturbations of f , $\hat{a}$ and $\hat{h}$ [Yeh et al., 1985a] is:

$$\hat{h}(\Theta) = \frac{j \underline{k} \cdot \underline{J} [\hat{f} - H(\Theta) \hat{a}] - (\underline{J} \cdot \underline{J} - J_1) \hat{a}}{k^2 + jA(2\underline{k} \cdot \underline{J} - k_1)} \quad (1.7)$$

where $\underline{k}=(k_1, k_2, k_3)$ is the wave number vector, $k=|\underline{k}|$ and j is the imaginary unit.

In a similar vein, by linearization of Darcy's law for unsaturated flow, expressing the velocity in terms of mean, $\underline{U}$ and perturbation, $\underline{u}$, utilizing Taylor's expansion and retaining first-order terms, we have:

$$U_i = K_g(\Theta) J_i / n \Theta \quad (1.8a)$$

$$u_i = (K_g(\Theta) / n \Theta) \{ J_i [f - aH(\Theta) - Ah(\Theta)] + [\partial h(\Theta) / \partial x_i] \} \quad (1.8b)$$

where both porosity, n and water saturation, $\Theta = \Theta(H)$ are considered as deterministic constants and $K_g(\Theta) = \exp[F - AH(\Theta)]$ is the geometric mean conductivity.

Inasmuch as for a given water saturation, Θ , $\log K(\Theta)$ is MVN, and $\psi(\Theta)$, through the linearization of the flow equation, is a linear function of $\log K(\Theta)$, it follows that for a given Θ , $\psi(\Theta)$ is also MVN. Then by (1.8), for a given Θ , so is the velocity, characterized completely by the mean, U_i , $i=1,2,3$, and the covariance tensor, $u_{ij}(\xi)$ ($i,j=1,2,3$). In the following, first-order approximations of $u_{ij}(\xi; \Theta)$ will be derived.

Representing the perturbed term (1.8b) by the stochastic Fourier transform integral, the relationship among the Fourier amplitudes of the perturbations of $\hat{u}_i$, f , $\hat{a}$ and $\hat{h}$ is:

$$\hat{u}_i = (K_g(\Theta) / n \Theta) \{ J_i [f - \hat{a}H(\Theta) - A\hat{h}(\Theta)] + j k_i \hat{h}(\Theta) \} \quad (1.9)$$

Substituting (1.7) in (1.9), multiplying both sides of the resultant by the complex conjugate of the Fourier amplitude, $\hat{u}_i$, taking mean values and using the "spectral representation" theorem, we obtain the corresponding expression for the spectrum:

$$\hat{u}_{ij}(\underline{k}; \Theta) = \sum_{p=1}^3 c_p \hat{C}_{pp}(\underline{k}) \sum_{q=1}^3 \sum_{r=1}^3 U_q U_r (\delta_{qi} - \frac{k_i k_q}{k^2 + jA(2\underline{k} \cdot \underline{J} - k_1)}) (\delta_{rj} - \frac{k_j k_r}{k^2 + jA(2\underline{k} \cdot \underline{J} - k_1)}) \quad (1.10)$$

where $p=1,2,3$ for f, a and fa, respectively, $c_1=1$, $c_2=H^2(\Theta) + (\underline{J} \cdot \underline{J} - J_1)^2$, $c_3=-2H(\Theta)$, δ is the Kronecker delta, and $\hat{C}_{pp}(\underline{k})$ is the inverse Fourier transform of (1.4) given [Bakr et al., 1978] by:

$$\hat{C}_{pp}(\underline{k}) = \frac{\sigma_p^2 I_{p1} I_{p2} I_{p3}}{\pi^2 (1 + I_{p1}^2 k_1^2 + I_{p2}^2 k_2^2 + I_{p3}^2 k_3^2)^2} \quad (1.11)$$

where $p=f, a$ or fa .

For a mean gradient that exists only in the x_1 direction, i.e., $\underline{J}=(J_1, 0, 0)$, the spectrum of the velocity covariance tensor is obtained by substituting (1.11) in (1.10) (for $q=1$ and $r=1$, only), i.e.,

$$\hat{u}_{ij}(\underline{k}; \Theta) = U^2 \sum_{p=1}^3 \frac{c_p \sigma_p^2 I_{p1} I_{p2} I_{p3}}{\pi^2 (1 + I_{p1}^2 k_1^2 + I_{p2}^2 k_2^2 + I_{p3}^2 k_3^2)^2} (\delta_{1i} - \frac{k_i k_1}{k^2 + jBk_1}) (\delta_{1j} - \frac{k_j k_1}{k^2 + jBk_1}) \quad (1.12)$$

where $U=|\underline{U}|$, $\underline{U}=K_g(\Theta)\underline{J}/n\Theta$, $B=(2J_1-1)A$ and c_2 simplifies to $c_2=H^2(\Theta)$.

For heterogeneous porous formations of axisymmetric anisotropy, with mean flow in the vertical direction, perpendicular to the bedding, i.e., $I_{p2}=I_{p3}=I_{ph}$, $I_{p1}=I_{pv}$, $e_{p2}=e_{p3}=1/e_p$, $e_p=I_{pv}/I_{ph}$, expressing the scaled wave number vector $\underline{k}'_p$ in terms of the spherical coordinates system (k'_p, ϕ, β) ((A4)) and the scaled separation vector, $\underline{\xi}'_p$, in terms of the spherical coordinates (ξ'_p, θ, χ) ((A6)), the Fourier transform of the spectrum $\hat{u}_{ij}(\underline{k})$ (1.12) (see Appendix A) is:

$$u_{ij}(\xi, \theta, \chi; \Theta) = U^2 \sum_{p=1}^3 \frac{c_p \sigma_p^2}{4\pi} \int_0^{2\pi} \int_0^\pi c_{ij}^p \left(\frac{a_p}{b_p^2} \right) \sin\phi d\phi d\mu \quad (1.13a)$$

where ϕ is the angle between $\underline{k}'_p$ and the k'_{p1} coordinate, μ is the angle between the projection of $\underline{k}'_p$ on the $k'_{p2}k'_{p3}$ plane and the k'_{p2} coordinate, and $k'_p = |\underline{k}'_p|$; χ is the angle between ξ'_p and the ξ'_{p1} coordinate, θ is the angle between the projection of ξ'_p on the $\xi'_{p2}\xi'_{p3}$ plane and the ξ'_{p2} coordinate, and $\xi'_p = |\xi'_p|$; a_p is given by:

$$a_p = \frac{[(1 - |r_p| \xi'_p)(\sin^2\phi + e_p^{-2} \cos^2\phi)^2 - (3 - |r_p| \xi'_p) e_p^{-4} \cos^2\phi g_p^2]}{\exp(|r_p| \xi'_p)} + \frac{2 \cos^3\phi e_p^{-6} g_p^3}{(\sin^2\phi + e_p^{-2} \cos^2\phi)} \exp\left[-\frac{e_p^{-2} \cos\phi g_p |r_p| \xi'_p}{\sin^2\phi + e_p^{-2} \cos^2\phi}\right] \quad (1.13b)$$

$r_p = \cos\nu_p$ with ν_p the angle between ξ'_p and $\underline{k}'_p$, given by (A7); b_p^2 is given by:

$$b_p^2 = [(\sin^2\phi + e_p^{-2} \cos^2\phi)^2 - e_p^{-4} \cos^2\phi g_p^2]^2 \quad (1.13c)$$

$g_p = (2J_1 - 1)AI_{p1}$ and the c_{ij}^p ($i, j = 1, 2, 3$) terms are given by (A11) with b_p^2 given by (1.13c) instead of (A12). Note that without loss of generality, J_1 is taken in the remainder of this chapter as unity.

Dimensionless forms of (1.13), independent of water saturation, Θ , are obtained by dividing both their sides by $\sigma_y^2(\Theta)U^2$, and by dividing the separation vector, ξ , by $I_y(\Theta)$, i.e., $u'_{ij} = u_{ij}/\sigma_y^2(\Theta)U^2$, ($i, j = 1$ to 3), and $\xi' = |\xi'|$, $\xi' = \xi/I_y(\Theta)$, where $\sigma_y^2(\Theta) = C_{yy}(0; \Theta)$ and $I_{y1}(\Theta) = \int_0^\infty C_{yy}(\xi; \Theta) d\xi / C_{yy}(0; \Theta)$ ($i = 1$ to 3) are log-unsaturated conductivity variance and correlation scales, respectively.

1.1.2 First-Order Approximation of the Displacement Covariance Tensor

Using a general Lagrangian description of the motion of a solute particle by steady-state flow, the particle trajectory, $\underline{X}(t)$, is the solution of the kinematic equation $d\underline{X}/dt = \underline{V}(\underline{X})$, with $\underline{X} = \underline{a}$ for $t=0$, where $\underline{V} = \underline{U} + \underline{u}$ is the Eulerian velocity, $\underline{U} = \langle \underline{V} \rangle$ is its expected value, assumed to be constant, uniform in space and time, and $\underline{u}$ is its fluctuation. Neglecting pore scale dispersion, for a solute particle injected into the flow field at time $t=0$ and location $\underline{X} = \underline{a}$, $\underline{a} = (a_1, a_2, a_3)$ within a release volume, Ω_0 , the trajectory $\underline{X} = (X_1, X_2, X_3)$ at time t is given [Dagan, 1989] by:

$$\underline{X}(t; \underline{a}) = \underline{a} + \underline{U}t + \int_0^t \underline{u}[\underline{X}(t'; \underline{a})] dt' \quad (1.14)$$

Because $\underline{u}(t) = \underline{u}[\underline{X}(t; \underline{a})]$, the nonlinearity of the integral on the RHS of (1.14), does not allow explicit expression for the relationships between the statistical moments of the PDF of the Lagrangian particle displacement, $\underline{X}$ and those of the Eulerian velocity PDF. Assuming ergodic conditions and Lagrangian and Eulerian stationarity and homogeneity, Dagan [1982, 1984] overcame this difficulty by approximating the actual trajectory of the particle path by its mean path. In other words, the actual trajectory in the argument of $\underline{u}$ in (1.14) is replaced by its mean, i.e.,

$$\underline{X}(t; \underline{a}) = \underline{a} + \underline{U}t + \int_0^t \underline{u}(\underline{U}t') dt' \quad (1.15)$$

Under the aforementioned assumptions, for fixed $\underline{a}$, the particle displacement mean, $\langle \underline{X}(t) \rangle$ and, by a first-order approximation in the velocity variance, the particle displacement covariance, $X_{ij}(t) = \langle X'_i(t) X'_j(t) \rangle$, $(i, j = 1, 2, 3)$, at time t , where $\underline{X}' = \underline{X} - \langle \underline{X} \rangle$

is the fluctuation, are given [Dagan, 1989] by:

$$\langle \underline{X}(t) \rangle = \underline{U}t \quad (1.16a)$$

$$X_{ij}(t) = \int_0^t \int_0^t u_{ij}(\underline{U}t', \underline{U}t'') dt' dt'' \quad (1.16b)$$

where for simplicity the particle location at $t=0$ is taken here as $\underline{a}=0$.

Eqs. (1.16a) and (1.16b) are of general nature, independent of flow conditions, (i.e., whether it is saturated or unsaturated), consistent with the linearization of the flow equation, and have been used in the past to model transport under saturated groundwater [e.g., Dagan, 1984, 1988], and vadose-zone [Russo, 1993] flows. It should be emphasized, however, that (1.16b) is restricted to flow regimes associated with relatively large Peclet numbers UI_{y1}/D_L , $UI_{y2}/I_{y1}D_T$ and $UI_{y3}/I_{y1}D_T$ [Dagan, 1988], where D_L and D_T are the longitudinal and transverse components of the pore scale dispersion tensor.

For a multivariate normal (MVN) Eulerian velocity field, so is $\underline{X}(t)$, the PDF of which is completely defined by the mean vector, $\langle \underline{X}(t) \rangle$, and the covariance tensor, $X_{ij}(t)$ ($i, j=1, 2, 3$). From a physical point of view, the ratios $X_{ij}/2t$ may be regarded as the apparent dispersion coefficients, that would lead to the same X_{ij} as the actual time dependent ones in the solution of the convection-dispersion equation with constant coefficients. For $t \rightarrow \infty$, these ratios tend to the constant macrodispersion coefficients obtained from:

$$D_{ij}(t) = \frac{1}{2} \left[\frac{dX_{ij}(t)}{dt} \right] \quad (i, j = 1, 2, 3) \quad (1.17)$$

Components of the displacement covariance tensor, X_{ij} and the macrodispersion tensor, D_{ij} for mean flow in an arbitrary direction with respect to the principal axes of the formation heterogeneity are obtained by integrating the respective components of the velocity

covariance tensor, u_{ij} ((13)) along a line inclined to the mean gradient. To do so, the original coordinate system $\underline{x}=(x_1, x_2, x_3)$ is transformed by a rotation about the origin to a new coordinate system $\underline{x}'=(x'_1, x'_2, x'_3)$, such that x'_1 is parallel with the mean gradient vector $\underline{J}$. Using the Euler angles α', β', γ' (Fig. 1.2b) the components of $\underline{J}$ along the axes of the original coordinate system are given [Margenau and Murphy, 1964] by $J_1 = J \cos \beta'$, $J_2 = J \sin \beta' \sin \alpha'$ and $J_3 = -J \sin \beta' \cos \alpha'$, where $J = |\underline{J}|$, α' is the angle between the x_2 axis and the intersection of the $x_2 o x_3$ and the $x'_2 o x'_3$ planes (the axis $o p$, Fig. 1.1b) and β' is the angle between x_1 and x'_1 . Note that x_1, x_2 and x_3 are the principal axes of the log-conductivity covariance, $C_{yy}(\xi; \Theta)$ the correlation scales of which are I_{yv} , I_{yh} and I_{yh} , respectively.

The coordinates of $\underline{J}$ (J, α', β') are superimposed on the coordinates of the scaled wave number vector, $\underline{k}'_p$ (k'_p, ϕ, μ) ((A4)) in such a way that the J_1 coordinate coincides with the k'_{p1} coordinate, with ζ_p , the angle between $\underline{J}$ and $\underline{k}'_p$, (see Fig. 1.1b) given by:

$$\zeta_p = \cos^{-1}[\cos \beta' \cos \phi + e_p(\sin \beta' \cos \alpha' \sin \phi \cos \mu + \sin \beta' \sin \alpha' \sin \phi \sin \mu)] \quad (1.18)$$

Using $\xi = Ut$ and $r'_p = \cos \zeta_p$ rather than $r_p = \cos \nu_p$ in (1.13) and substitution the resultant in (1.16b) employing the Cauchy algorithm, the displacement covariance tensor, $X_{ij}(t, \alpha', \beta'; \Theta)$, ($i, j = 1, 2, 3$), is given by:

$$X_{ij}(t, \alpha', \beta'; \Theta) = \sum_{p=1}^3 \frac{c_p I_{p1}^2 \sigma_p^2}{2\pi} \int_0^{2\pi} \int_0^\pi c_{ij}^p \left(\frac{a'_p}{b_p^2} \right) \sin \phi d\phi d\mu \quad (1.19a)$$

where a'_p is given by

$$\begin{aligned}
a'_p = & \frac{[\exp(|r'_p| Ut) (\sin^2 \phi + e_p^{-2} \cos^2 \phi - e_p^{-2} \cos \phi g_p)^2 - (\sin^2 \phi + e_p^{-2} \cos^2 \phi)^2 (1 + |r'_p| Ut)]}{r_p'^2 \exp(|r'_p| Ut)} \\
& - \frac{(e_p^{-4} \cos^2 \phi g_p^2)(1 - |r'_p| Ut)}{r_p'^2 \exp(|r'_p| Ut)} + \frac{2 e_p^{-2} \cos \phi g_p (\sin^2 \phi + e_p^{-2} \cos^2 \phi)}{r_p'^2 \exp[\frac{e_p^{-2} \cos \phi g_p |r'_p| Ut}{\sin^2 \phi + e_p^{-2} \cos^2 \phi}]} \quad (1.19b)
\end{aligned}$$

The respective macrodispersion tensor, $D_{ij}(t, \alpha', \beta'; \Theta)$, ($i, j=1, 2, 3$) is calculated by substitution of (1.19) in (1.17), i.e.,

$$D_{ij}(t, \alpha', \beta'; \Theta) = U \sum_{p=1}^3 \frac{c_p I_{p1} \sigma_p^2}{4\pi} \int_0^{2\pi} \int_0^\pi c_{ij}^p \left(\frac{a''_p}{b_p^2} \right) \sin \phi d\phi d\mu \quad (1.20a)$$

where a''_p is given by

$$\begin{aligned}
a''_p = & \frac{[(\sin^2 \phi + e_p^{-2} \cos^2 \phi)^2 |r'_p| Ut + e_p^{-4} \cos^2 \phi g_p^2 (2 - |r'_p| Ut)]}{|r'_p| \exp(|r'_p| Ut)} \\
& - \frac{2 e_p^{-4} \cos^2 \phi g_p^2}{|r'_p| \exp[\frac{e_p^{-2} \cos \phi g_p |r'_p| Ut}{\sin^2 \phi + e_p^{-2} \cos^2 \phi}]} \quad (20b)
\end{aligned}$$

Dimensionless forms of (1.19) and (1.20), independent of water saturation, are obtained by dividing both their sides by $\sigma_y^2(\Theta) I_{y1}^2(\Theta)$, and $\sigma_y^2(\Theta) I_{y1}(\Theta) U$, respectively, i.e., $X'_{ij} = X_{ij} / \sigma_y^2(\Theta) I_{y1}^2(\Theta)$ and $D'_{ij} = D_{ij} / \sigma_y^2(\Theta) I_{y1}(\Theta) U$, ($i, j=1$ to 3), and by expressing time as $t' = tU / I_{y1}(\Theta)$.

It should be emphasized that for given statistics of the perturbations of the $\log K_s$ and α fields, the resultant normalized velocity covariance tensor $u'_{ij}(\xi', \theta, \chi)$, and, concurrently, $X'_{ij}(t', \alpha', \beta')$ and $D'_{ij}(t', \alpha', \beta')$, depend on both $A = \langle \alpha \rangle$ and $e = I_{yv} / I_{yh}$. For fixed I_{yv} , at

the small limit of A , $A \rightarrow 0$ they converge to their counterparts under saturated flow.

1.2 Results and Discussion

1.2.1 The Velocity Covariance Tensor

First-order approximations of the components of the dimensionless velocity covariance tensor in the spherical coordinate system (A4), $u'_{ij}(\xi', \theta, \chi)$, ($i, j = 1, 2, 3$), as functions of the scaled separation distance, ξ' , for various combinations of the angles θ and χ , calculated from (13), for two different values of the anisotropy ratio, $e = I_{yv}/I_{yh}$, (where $I_{yv} = I_{y1}(\Theta)$, $I_{yh} = I_{y2}(\Theta) = I_{y3}(\Theta)$) and $AI_{yv} = 0.05$, are depicted in Figs. 1.2 and 1.3. Note that the components of $u'_{ij}(\xi')$ depicted in these figures are consistent with their counterparts for saturated flow with mean gradient parallel to the formation bedding [Rubin and Dagan, 1992]. The main features of the components of $u'_{ij}(\xi')$, ($i, j = 1, 2, 3$), are summarized as follows:

(i) Due to the isotropy in the x_2x_3 plane, $u'_{11}(\xi', \theta, \chi)$ is independent of the angle θ between the projection of ξ' on the x_2x_3 plane and the x_2 axis, while $u'_{33}(\xi', \theta, \chi) = u'_{22}(\xi', \pi/2 - \theta, \chi)$, $u'_{13}(\xi', \theta, \chi) = u'_{12}(\xi', \pi/2 - \theta, \chi)$ and $u'_{23}(\xi', \theta, \chi) = u'_{23}(\xi', \pi/2 - \theta, \chi)$.

(ii) The principal components of u'_{ij} , $u'_{ii}(\xi')$, $i = 1, 2, 3$, are symmetric with respect to each of the three components of the scaled separation vector, ξ' . The off-diagonal components of u'_{ij} , $u'_{12}(\xi')$ and $u'_{13}(\xi')$ are symmetric only with respect to ξ'_1 , while $u'_{23}(\xi')$ is asymmetric with respect to each of the three components of ξ' .

(iii) When the scaled separation vector, ξ' coincides with the x_1 axis, (i.e., the direction of the mean flow, $\chi = 0$) and also when $\chi > 0$, the longitudinal component of u'_{ij} , $u'_{11}(\xi', \theta, \chi)$ is positive; it may exhibit negative values, however, when ξ' is aligned in the x_2x_3 plane ($\chi = \pi/2$). When ξ' coincides with the x_1 axis, ($\chi = 0$) and when ξ' coincides with the x_i axes,

$i=2,3$, the respective transverse components of u'_{ij} , $u'_{ii}(\xi', \theta, \chi)$, $i=2,3$, are "hole" functions having zero correlation scales; they may have nonzero correlation scales, however, when ξ' is inclined to the principal axes of the formation heterogeneity.

(iv) The cross-covariances between the longitudinal and transverse components of $\underline{u}$, $u'_{12}(\xi', \theta, \chi)$ and $u'_{13}(\xi', \theta, \chi)$, are nonnegative, while the cross-covariance between the transverse components of $\underline{u}$, $u'_{23}(\xi', \theta, \chi)$ is negative when ξ' is inclined to the x_1 axis at angles that exceed $\chi = \pi/4$.

(v) For a given anisotropy ratio, e , $u'_{11}(\xi')$ is most persistent when ξ' coincides with the x_1 axis ($\chi=0$) and least persistent when ξ' is inclined to the x_1 axis at angle $\chi = \pi/2$, while $u'_{ii}(\xi'; \theta)$, $i=2,3$, are most persistent when ξ' coincides with the x_j axes, $j=3,2$, respectively, (i.e., $\chi = \pi/2$, $\theta = \pi/2$, and $\chi = \pi/2$, $\theta = 0$, respectively) and are least persistent when ξ' coincides with the x_1 axis ($\chi=0$). Both magnitude and persistence of the off-diagonal components of u'_{ij} , $u'_{ij}(\xi')$, $i,j=1$ to 3 , $i \neq j$, have their peak values when ξ' coincides with the 45° lines in the respective $x_i x_j$ planes; they vanish when ξ' coincides with the x_i axes, $i=1$ to 3 .

(vi) For a given alignment of ξ' relative to the direction of the mean flow, the persistence of the components of $u'_{ij}(\xi')$ increases with increasing anisotropy (decreasing e). Peak values of the principal components of $u'_{ij}(\xi')$ occur at the small limit of $\xi' = |\xi'|$, $\xi' \rightarrow 0$, and, in turn, are monotonically increasing functions of e ($u'_{11}(0)$), or nonmonotonic functions of e ($u'_{ii}(0)$, $i=2,3$) [Russo, 1995a]. Peak values of the off-diagonal components of $u'_{ij}(\xi')$ occur at nonzero ξ' and are nonmonotonic functions of e .

Interpretation of the behavior of the $u'_{ij}(\xi')$ tensor is facilitated by referring to the first-order approximation of the velocity fluctuation, u_i , $i=1$ to 3 (1.8b). For mean flow parallel to the x_1 axis, the first term of u_i , i.e., $[K_g(\theta)/n\theta]\{J_i[f-aH(\theta)-Ah(\theta)]\}$ is zero for $i=2,3$ and

is responsible for the variations in the velocity in the direction of the mean flow, because the conductivity, equal at first order to $[K_g(\Theta)/n\Theta][1+f-aH(\Theta)-Ah(\Theta)]$, varies along the streamtubes. The second term of u_i , namely, $-[K_g(\Theta)/n\Theta][\partial h(\Theta)/\partial x_i]$, $i=1,2,3$, is responsible for the winding of the streamtubes and for the change of their cross-section [Dagan, 1989]. The first term of u_1 decreases, while its second term increases as ξ is more inclined to the x_1 axis. The second terms of u_i , $i=2,3$, increase as ξ is more inclined to the x_1 -axis and to the x_i , $i=2,3$ axes, respectively. Furthermore, for a fixed log-conductivity correlation scale in the direction of the mean flow, the first term of u_1 decreases, while the second terms of u_i , $i=1,2,3$, increase with decreasing e .

1.2.2 The Displacement Covariance Tensor

First-order approximations of the components of the dimensionless displacement covariance tensor, X'_{ij} , ($i,j=1,2,3$), for the case where the mean gradient vector, $\underline{I}$ is inclined at arbitrary angles β' and α' with the principal axes of the formation heterogeneity, as functions of the scaled time, $t'=tU/I_{yv}$, calculated from (1.19), for two different values of the anisotropy ratio, e and $AI_{yv}=0.05$, are depicted in Figs. 1.4 and 1.5. The main characteristics of the components of $X'_{ij}(t',\alpha',\beta')$, ($i,j=1,2,3$), are summarized as follows:

(i) Because $C_{yy}(\xi;\Theta)$ is axisymmetric, $X'_{11}(t',\alpha',\beta')$ is independent of the angle α' while $X'_{33}(t',\alpha',\beta')=X'_{22}(t',\pi/2-\alpha',\beta')$, $X'_{13}(t',\alpha',\beta')=X'_{12}(t',\pi/2-\alpha',\beta')$ and $X'_{23}(t',\alpha',\beta')=X'_{23}(t',\pi/2-\alpha',\beta')$.

(ii) The principal components of X'_{ij} are independent of the quadrants of either α' or β' . On the other hand, the off-diagonal components of X'_{ij} , X'_{12} and X'_{13} depend on the quadrant of α' , while X'_{23} depends on the quadrants of both α' and χ .

(iii) For a given anisotropy ratio, e the magnitude of the longitudinal component of X'_{ij} ,

$X'_{11}(t', \alpha', \beta')$ decreases and its evolution at a rate faster than linearly in t' persists for smaller travel time as the angle β' between $\underline{l}$ and the x_1 axis increases. The transverse components of X'_{ij} , $X'_{ii}(t', \alpha', \beta')$, $i=2,3$, approach asymptotic values, when $\underline{l}$ is parallel to the x_1 axis ($\beta'=0$, $\underline{l}=(1,0,0)$), and when $\underline{l}$ is parallel to the x_i axes, $i=2,3$, respectively ($\beta'=\pi/2$, $\alpha'=0$, $\underline{l}=(0,1,0)$ and $\beta'=\pi/2$, $\alpha'=\pi/2$, $\underline{l}=(0,0,1)$, respectively). When $\underline{l}$ is inclined to the principal axes of the formation heterogeneity with arbitrary angles, $0 < \beta' < \pi/2$ and $0 < \alpha' < \pi/2$, however, for a given β' , the magnitudes of $X'_{22}(t', \alpha', \beta')$ and $X'_{33}(t', \pi/2 - \alpha', \beta')$ increase and their evolution at a rate faster than linearly in t' persist for larger travel time, as the angle α' increases.

(iv) For a given e , the off-diagonal components of X'_{ij} , $X'_{ij}(t', \alpha', \beta')$, $i, j=1,2,3$, $i \neq j$, vanish when $\underline{l}$ is parallel to each of the x_i axes, $i=1,2,3$, while their maximum absolute values occur when $\underline{l}$ coincides with the 45° lines in the respective $x_i x_j$ planes. For a given $\beta' > 0$, the magnitudes of the cross-covariances between the longitudinal and transverse components of $\underline{X}'$, $X'_{12}(t', \alpha', \beta')$ and $X'_{13}(t', \pi/2 - \alpha', \beta')$ increase and their evolution at rate faster than linearly in t' persist for larger travel time as the angle α' decreases. The cross-covariance between the transverse components of $\underline{X}'$, $X'_{23}(t', \alpha', \beta')$ is negative when $\underline{l}$ is inclined to the x_1 axis at angles that exceed $\beta' = \pi/4$. For a given $\alpha' > 0$, the absolute magnitude of $X'_{23}(t', \alpha', \beta')$ increases and its evolution at rate faster than linearly in t' persists for larger travel time as the angle β' increases.

(v) For a given alignment of $\underline{l}$ relative to the principal axes of $C_{yy}(\underline{x}; \Theta)$, and for a given t' , the magnitude of X'_{11} decreases, while the magnitudes of X'_{ii} , $i=2,3$, and the off-diagonal components of X'_{ij} increase with decreasing e . Furthermore, the evolution of each of the components of X'_{ij} at a rate faster than linearly in t' persists for a larger travel time as e decreases; for the case where $\underline{l}$ is parallel to the x_1 axis, or when $\underline{l}$ is parallel to each of the

x_i axes, $i=2,3$, the respective X'_{ii} , $i=2,3$, components tend asymptotically to constant values more slowly, as e decreases.

1.2.3 Asymptotic Macrodispersion Coefficients

Asymptotic constant macrodispersion coefficients, D_{ij} ($i,j=1,2,3$) for a mean flow in an arbitrary direction with respect to the principal axes of the formation heterogeneity can be calculated from (1.20) taking the limit $t \rightarrow \infty$. This is equivalent to integrating the velocity covariance tensor, u'_{ij} along a line inclined to the mean gradient vector, i.e.,

$$D_{ij}(\alpha', \beta'; \Theta) = U \int_0^\infty u'_{ij}(\xi', \alpha', \beta'; \Theta) d\xi' \quad , (i, j = 1, 2, 3) \quad (1.21)$$

The dimensionless macrodispersion coefficients, $D'_{ij}(\alpha', \beta') = D_{ij}(\alpha', \beta'; \Theta) / U \sigma_y^2(\Theta) I_{y1}(\Theta)$, $i, j=1,2,3$ are independent of water saturation, Θ , and are demonstrated in Fig. 1.6 as functions of the angles β' and α' , for $e=1$ and for three different values of $A = \langle \alpha \rangle$. At the small A limit, $A \rightarrow 0$ and for $\alpha' = 0$, they are consistent with their counterparts for saturated flow with mean gradient, $\underline{I} = (J_1, 0, J_3)$ inclined at angle β' to the formation bedding [Gelhar and Axness, 1983]. Note that due to the isotropy in the x_2x_3 plane, $D'_{11}(\alpha', \beta')$ is independent of the angle α' , while $D'_{22}(\alpha', \beta') = D'_{33}(\pi/2 - \alpha', \beta')$, $D'_{13}(\alpha', \beta') = D'_{12}(\pi/2 - \alpha', \beta')$ and $D'_{23}(\alpha', \beta') = D'_{23}(\pi/2 - \alpha', \beta')$.

When $\underline{I}$ coincides with the x_1 axis (i.e., $\beta' \rightarrow 0$), by continuity considerations, the RHS of (1.21) (for $i,j=1$) must equal $\sigma_y^2(\Theta) I_{y1}(\Theta) U$; consequently, for $\beta' = 0$, the longitudinal component of D'_{ij} , D'_{11} , equals unity independent of e , while for $\beta' > 0$, D'_{11} decreases monotonically with β' at a rate that increases with decreasing e and increasing A (for fixed I_{yv}). Similarly, for the transverse components of D'_{ij} , D'_{ii} , $i=2,3$, by continuity

considerations, when $\underline{I}$ coincides with the x_1 axis, and the x_i axes, $i=2,3$, respectively, the RHS of (1.21) (for $i=2,3$, $j=i$) must vanish; consequently $D'_{ii}(\alpha''=0, \beta'=0)$ and $D'_{ii}(\alpha''=0, \beta'=\pi/2)$, $i=2,3$, are zero independent of e , where $\alpha''=\alpha'$ and $\alpha''=\pi/2-\alpha'$ for D'_{22} and D'_{33} , respectively. For other combinations of α' and β' , however, the transverse components of D'_{ij} are nonzero, either nonmonotonic (for $\alpha'' \leq \pi/4$) or increasing monotonic (for $\alpha'' > \pi/4$) functions of β' . For a given α' , the rate of change of D'_{ii} , $i=2,3$, with β' increases with decreasing e and decreasing A (for fixed I_{yv}).

For $e=1$ and $A \rightarrow 0$, when $\beta' \rightarrow \pi/2$, (i.e., when $J_1 \rightarrow 0$), $D'_{11}=3/8$, while for $\alpha''=\pi/2$ and $\beta'=\pi/2$ (i.e., when $J_1=J_3=0$ or when $J_1=J_2=0$) $D'_{22}=D'_{33}=1/8$. Furthermore when β' equals $\beta'_1 = \tan^{-1}(\sqrt{2})$ (i.e., when $J_1 = \sqrt{(J_2^2 + J_3^2)/2}$), D'_{22} and D'_{33} are independent of α' and equal to $1/12$ while $D'_{11}=1/2$. Both the value of β'_1 and the ratio $D'_{22}(\beta'_1)/D'_{11}(\beta'_1)$ decrease with increasing A and increase with decreasing e .

The off-diagonal components of D'_{ij} , $D'_{12}(\alpha', \beta')$ and $D'_{13}(\alpha', \beta')$ are monotonic functions of α' and nonmonotonic functions of β' . They vanish when $\underline{I}$ coincides with each of the x_i , $i=1,2,3$ axes and also at an intermediate value of $\beta'=\beta'_2$ when $AI_{yv} > \approx 0.7$, exhibiting negative values when $\beta' > \beta'_2$. For a given I_{yv} , the value of β'_2 decreases with increasing A and increases with decreasing e , indicating that D'_{12} and D'_{13} change their signs at smaller inclination of $\underline{I}$ as both A and e increase. The off-diagonal component $D'_{23}(\alpha', \beta')$ is a nonmonotonic function of both β' and α' and vanishes when $\underline{I}$ coincides with the x_1 axis ($\beta'=0$) and at the value of $\beta'=\beta'_1$ for which D'_{22} and D'_{33} are independent of the value of α' . Inasmuch as the value of β'_1 decreases with increasing A and increases with decreasing e , D'_{23} changes its sign at smaller inclination of $\underline{I}$ as both A and e increase.

For $e=1$ and $A \rightarrow 0$, maximum values of D'_{12} and D'_{13} occur when $\beta' = \tan^{-1}((4/9)\sqrt{2})$, (i.e., when $J_1 = (9/4)\sqrt{(J_2^2 + J_3^2)/2}$) while the maximum and minimum (negative) values of

D'_{23} occur when $\beta' = \tan^{-1}(\sqrt{2}/2)$ and $\beta' \rightarrow \pi/2$ (i.e., when $J_1 = 2\sqrt{(J_2^2 + J_3^2)}/2$ and $J_1 = 0$), respectively. For fixed I_{yv} and for given β' and α' , the positive values of D'_{12} and D'_{13} and the absolute values of D'_{23} decrease with increasing A and increase with decreasing e , while the converse is true for the negative values of D'_{12} and D'_{13} .

The aforementioned results indicate that the principal axes of the macrodispersion tensor coincide with the direction of the mean flow, only when $\underline{J}$ coincides with the principal axes of the formation heterogeneity. Nonzero off-diagonal components of D'_{ij} imply that the principal axes associated with the principal components of D'_{ij} are deflected relative to the direction of the mean gradient, that, in turn, is inclined to the principal axes of the log-conductivity covariance, $C_{yy}(\xi; \Theta)$. Positive D'_{12} (and/or D'_{13}) means that the principal axes associated with the principal components of the macrodispersivity tensor are deflected in the same direction as that of $\underline{J}$ relative to the principal axes of C_{yy} , while the converse is true for negative D'_{12} and/or D'_{13} .

1.2.4 Effect of Mean Water Saturation on u_{ij} and D_{ij}

The effect of mean water saturation on the components of the velocity covariance tensor, $u_{ij}(\xi, \theta, \chi; \Theta)$ and the macrodispersion tensor, $D_{ij}(t, \alpha', \beta')$ is due to its effect on the log-unsaturated conductivity variance, $\sigma_y^2(\Theta)$ and correlation scales, $I_{yi}(\Theta)$, $i=1,2,3$. For given $A = \langle \alpha \rangle$ and $e = I_{yv}/I_{yh}$, denoting $u_{ij}^*(\xi^*, \theta, \chi; \Theta^*) = U^2 u_{ij}(\xi', \theta, \chi) \sigma_y^2(\Theta^*)$ and $D_{ij}^*(t^*, \alpha', \beta'; \Theta^*) = U D_{ij}(t', \alpha', \beta') \sigma_y^2(\Theta^*) I_{y1}(\Theta^*)$ as u_{ij} and D_{ij} , respectively, at a reference water saturation, Θ^* , where $\xi^* = \xi' I_{y1}(\Theta^*)$ and $t^* = t' I_{y1}(\Theta^*)/U$, then, the velocity covariance tensor and the macrodispersion tensor at an arbitrary water saturation, Θ may be expressed similar to Russo [1995b] as:

$$u_{ij}(\xi, \theta, \chi; \Theta) = R_1(\Theta) u_{ij}^* \{[R_2(\Theta)\xi^*], \theta, \chi; \Theta^*\} \quad (1.22a)$$

$$D_{ij}(t, \alpha', \beta'; \Theta) = R_3(\Theta) D_{ij}^* \{[R_4(\Theta)t^*], \alpha', \beta'; \Theta^*\} \quad (1.22b)$$

where

$$R_1(\Theta) = \sigma_y^2(\Theta)/\sigma_y^2(\Theta^*) \quad (1.23a)$$

$$R_2(\Theta) = I_{y1}(\Theta)/I_{y1}(\Theta^*) \quad (1.23b)$$

$$R_3(\Theta) = \sigma_y^2(\Theta)I_{y1}(\Theta)/\sigma_y^2(\Theta^*)I_{y1}(\Theta^*) \quad (1.23c)$$

$$R_4(\Theta) = I_{y1}(\Theta)/I_{y1}(\Theta^*) \quad (1.23d)$$

Note that when $AI_{yv} < \approx 0.1$, u'_{ij} and D'_{ij} are essentially independent of A , and the reference water saturation can be taken as $\Theta^* = 1$ with $\sigma_y^2(\Theta^*) = \sigma_f^2$ and $I_{y1}(\Theta^*) = I_{f1}$. The coefficients $R_1(\Theta)$ and $R_3(\Theta)$ determine the magnitudes of $u_{ij}(\xi', \theta, \chi; \Theta)$ and $D_{ij}(t', \alpha', \beta'; \Theta)$, respectively, while the coefficients $R_2(\Theta)$ and $R_4(\Theta)$ determine the length of the velocity correlation scale, and how far the center of mass has to travel for $D_{ij}(t; \Theta)$ to approach their asymptotic values, $D_{ij}^\infty(\Theta)$, respectively, as compared with the flow conditions at the reference water saturation, Θ^* .

A detailed analysis of the dependence of the coefficients R_i , $i=1,2,3$, ((1.23)) on water saturation and on the statistics of the $\log K_s$ and the α fields in terms of the cross-correlation coefficient between $\log K_s$ and α , $\rho_{f\alpha}$, and the ratios between their correlation scales, $R_s = I_{a1}/I_{f1}$, and variabilities, $R_v = A^2 \sigma_a^2 / \sigma_f^2$, was presented recently [Russo, 1995b] for the case where $AI_{yv} < \approx 0.1$. The main results of this analysis reveal that for $\rho_{fa} \leq 0$, the coefficients R_1 and R_3 are monotonic decreasing functions, while R_2 and R_4 are monotonic increasing functions of water saturation, Θ . For $\rho_{fa} > 0$, the coefficients R_i , $i=1$ to 4, are nonmonotonic functions of Θ .

This means that for porous formation of given statistics, for $\rho_{fa} \leq 0$, the magnitudes of the

components of u_{ij} and D_{ij} in unsaturated flow are larger than that in saturated flow and increase with decreasing Θ . For $\rho_{fa} > 0$, u_{ij} and D_{ij} increase with decreasing Θ , when Θ is smaller than $\Theta_c(H_c)$, where H_c is given [Russo, 1995b] by $H_c = \rho_{fa} / \sqrt{R_v}$ and $H_c = 2\rho_{fa} / [\sqrt{R_v}(1+R_s)]$, respectively. For $I_a = I_f$, the rate at which $D_{ij} \rightarrow D_{ij}^\infty$ and the persistence of the components of u_{ij} are the same as in saturated flow irrespective of ρ_{fa} . For $I_a \neq I_f$ and $\rho_{fa} \leq 0$, the rate at which $D_{ij} \rightarrow D_{ij}^\infty$ increases and the persistence of the components of u_{ij} decreases with decreasing Θ when $I_a < I_f$, while the converse is true for $I_a > I_f$. The same is true for $\rho_{fa} > 0$ when Θ is smaller than $\Theta_c(H_c)$, where H_c is given [Russo, 1995b] by $H_c = \sqrt{R_v} \{ [(1-R_s^2)^2 + 4\rho_{fa}R_s^2]^{1/2} - (1-R_s^2) \} / 2\rho_{fa}R_s^2$, while the converse is true when Θ is greater than Θ_c .

1.2.5 Effect of Soil Texture

The dimensionless tensors u'_{ij} and D'_{ij} , and, concurrently, for a given water saturation, Θ , the tensors $u_{ij}(\Theta)$ and $D_{ij}(\Theta)$ depend on AI_{yv} . The product AI_{yv} can be interpreted as a length scale ratio, where I_{yv} characterizes the scale of heterogeneity in the vertical direction, while $\lambda = A^{-1}$, the macroscopic capillary length scale, characterizes the scale of the unsaturated flow. As was discussed by Russo [1995b], for fixed I_{yv} , the increase in $A = \langle \alpha \rangle$ expresses a transition from a fine-textured soil material, associated with significant capillary forces to a coarse-textured soil material, associated with negligible capillary forces. Therefore, as A increases, the capillary pressure head gradient fluctuations, $\partial h / \partial x_i$, $i = 1, 2, 3$, vanish and the flow becomes gravity dominated. Inasmuch as the first term of u_1 ((1.8b)), which dominates u_1 , decreases with A at a rate slower than that of $\partial h / \partial x_i$, $i = 2, 3$, the transverse components of u'_{ij} and D'_{ij} are more sensitive to changes in A as compared to the longitudinal components of u'_{ij} and D'_{ij} . The discrepancy between the sensitivity of u_1 and

u_i ($i=2,3$) to $A = \langle \alpha \rangle$, however, decreases with decreasing e .

For a given water saturation, Θ and fixed I_{yv} , the log-conductivity covariance, $C_{yy}(\xi; \Theta)$ ((1.5)) also depends on A . This is due to the fact that for a given Θ and given statistics of the $\log K_s$ and α fields, the joined contribution of the covariance of the capillary pressure head perturbation, $C_{hh}(\xi; \Theta)$ and the cross-covariance between perturbations of log-conductivity and capillary pressure head, $C_{yh}(\xi; \Theta) = C_{fh}(\xi; \Theta) - H(\Theta)C_{ah}(\xi; \Theta)$ to the log-conductivity covariance is given by $-A^2 C_{hh}(\xi; \Theta)$ [Russo, 1995b]. Because $\sigma_h^2(\Theta) = C_{hh}(0; \Theta)$ decreases with A at a rate smaller than quadratic in A , the product $A^2 \sigma_h^2(\Theta)$ increases and, consequently, $\sigma_y^2(\Theta) = C_{yy}(0; \Theta)$ decreases with increasing A . Inasmuch as the persistence of $C_{hh}(\xi; \Theta)$ decreases with increasing A , the persistence of $C_{yy}(\xi; \Theta)$ increases with increasing A . In other words, the log-conductivity correlation scales, $I_{yi}(\Theta) = \int_0^\infty C_{yy}(\xi; \Theta) d\xi / C_{yy}(0; \Theta)$ ($i=1$ to 3) increase with increasing A .

For given Θ and e , the effect of the soil texture on the components of the asymptotic macrodispersion tensor, D_{ij} , therefore, can be quantified by expressing the latter by:

$$D_{ij}(\alpha', \beta'; A; e; \Theta) = U D'_{ij}(\alpha', \beta'; A; e) \sigma_y'^2(A, e) \sigma_y''^2(\Theta) I'_y(A, e) I''_{yv}(\Theta) \quad (1.24)$$

where $D'_{ij}(\alpha', \beta'; A; e)$ is the nondimensional asymptotic macrodispersion tensor, $\sigma_y''^2(\Theta)$ and $I''_{yv}(\Theta)$ are log-conductivity variance and correlation scale for $A I_{yv} < \approx 0.1$, independent of A , given [Russo, 1995b] by:

$$\sigma_y''^2(\Theta) = \sigma_f^2 + H^2(\Theta) \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2 \quad (1.25a)$$

and $\sigma_y'(A, e) = \sigma_y^2(A, e; \Theta) / \sigma_y''^2(\Theta)$ and $I'_y(A, e) = I_y(A, e; \Theta) / I''_{yv}(\Theta)$, are Θ -independent,

$$I''_{yv}(\Theta) = \frac{\sigma_f^2 I_{f1} + H^2(\Theta) \sigma_a^2 I_{a1} - 2H(\Theta) \sigma_{fa}^2 I_{fa1}}{\sigma_f^2 + H^2(\Theta) \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2} \quad (1.25b)$$

scaled log-conductivity variance and correlation scale, respectively.

The scaled log-conductivity correlation scale, I'_y and variance, $\sigma_y'^2$ are depicted in Fig. 1.7 as functions of AI_{yv} for various values of $e = I_{yv}/I_{yh}$. For fixed I_{yv} , $\sigma_y'^2$ decreases with increasing A and decreasing e , while the converse is true for I'_y . The sensitivity of both $\sigma_y'^2$ and I'_y to A increases with decreasing e , because both the magnitude of $\sigma_h^2(\Theta)$ and the persistence of $C_{hh}(\xi; \Theta)$ increase with decreasing e .

1.3 Concluding Remarks

In this study we extend the earlier studies of transport by steady-state unsaturated flow in heterogeneous formations with three-dimensional, anisotropic structure [Russo, 1993; 1995b], by deriving first-order approximations of the principal and off-diagonal components of the velocity covariance tensor for the general case in which the separation vector, ξ is inclined to the mean gradient vector, $\underline{J}$ at arbitrary angles, taking into account the texture of the soil materials constituting the heterogeneous formation. The derived velocity covariance tensors, in turn, were employed for modeling transport in the vadose zone for the general case in which $\underline{J}$ is inclined to the principal axes of the formation heterogeneity at arbitrary angles by the use of a Lagrangian formulation.

It should be emphasized that the derived velocity covariance tensors can be employed to model transport taking into account the deviation of the solute particles from their mean path by using a particle-tracking method through conditional Monte Carlo simulations, as proposed by Rubin [1990] for transport under steady, two-dimensional, saturated flow. Inasmuch as

using a first-order approximation for the velocity covariance tensors and a nonlinear procedure for the particles trajectories is an inconsistent approximation, we did not pursue this line in this study. Rather, transport was modeled by using (1.16) which, in turn, is consistent with the linearization of the flow equation.

Regarding transport, the results of this study are consistent with the earlier studies [Russo, 1993; 1995b] of transport by steady-state, unsaturated flow in the sense that for porous formation of given statistics and a given texture (given A), the magnitude of the components of D_{ij} and the rate at which they approach their asymptotic values vary with water saturation, Θ in a manner which depends on the cross-correlation coefficient, ρ_{fa} and the correlation scales ratio, I_a/I_f . This means that generally, the magnitude of the components of D_{ij} in unsaturated flow will be larger as compared with saturated flow, and will increase faster with decreasing water saturation for negative ρ_{fa} and relatively large I_a/I_f .

New findings obtained in this study suggest that under unsaturated flow, for given statistics of the formation properties and given water saturation Θ , macrodispersion will diminish in formations of coarser texture, when the mean gradient vector, $\underline{J}$ does not coincide with the principal axes of the heterogeneous formation. In this case formations of coarser texture will diminish the deflection the principal axes associated with the principal components of the macrodispersion tensor, D_{ij} in the same direction as that of $\underline{J}$, and may enhance their deflection in a direction opposite to that of $\underline{J}$, relative to the principal axes of the formation heterogeneity. This means that in unsaturated flow, a decrease in the capillary forces (i.e., increasing A), may compensate for the enhanced lateral dispersion and the enhanced deflection of the principal axes of the principal components of D'_{ij} , due to an increase in $I_{yh}=I_{yv}/e$, i.e., an increase in the size of the typical flow barriers in the horizontal direction. Furthermore, the results of this study demonstrate that for a heterogeneous formation of

given statistics and texture and for a given Θ , the longitudinal component of the displacement covariance tensor decreases and its transverse components increase when $\underline{J}$ is more inclined to the longitudinal axis of the formation heterogeneity.

The later result is in qualitative agreement with results of numerical simulations of transport in partially saturated, heterogeneous formation under transient, nonmonotonic flow regimes, established by a periodic influx imposed on the entry zone [Russo et al., 1994]. The simulation results reveal an increase in the transverse component of $\underline{J}$ accompanying by a restricted longitudinal spreading and by an enhanced transverse spreading of the solute pulse with increasing Δt , where Δt is the extent of the redistribution periods between successive water applications. This finding is explained by the fact that during the redistribution periods, the flow regime is relaxed from the essentially unidirectional mean flow, (i.e., $J_2 \rightarrow 0$), imposed by the uniform influx during the infiltration periods. Consequently, during the former periods, the unsaturated conductivity and capillary pressure head gradients and, concurrently, the velocity are adjusted to the spatial heterogeneity in the formation properties, creating a multidimensional flow pattern, in which J_2 increases with increasing Δt .

Before conclusion of this chapter we would like to emphasize limitations of this study. The velocity covariance and displacement covariance tensors presented here were derived for an unbounded flow domain associated with constant mean head gradient, $\underline{J}$. For bounded flow situations such as a flow approaching a water table, in which $\underline{J}$ is not constant, however, the applicability of the results of this study will be restricted to situation where $\underline{J}$ varies slowly over log-conductivity correlation scale. Inasmuch as the scale of variation of the mean solution is given by the macroscopic capillary length scale, $\lambda = A^{-1}$, local stationary can be expected if $\lambda > \approx 10I_{yy}$ [Russo, 1995b]. Consequently, the stationary results are not expected to be valid for $AI_{yy} > \approx 0.1$ when $\underline{J}$ is not constant. Another limitation is due to the small

perturbations, first-order approximations of the velocity covariance tensor and the Lagrangian displacement tensor. Consequently, the results are formally limited to formations with log-unsaturated variances smaller than unity. The simplifying assumptions regarding the local flow (steady-state flow), the local unsaturated conductivity ((1.2)) and the constant and uniform in space Θ (for a given H), also might limit the applicability of the results of this study. A discussion of these limitations is given elsewhere [Russo, 1993; 1995b].

With these limitations in mind, we believe that the results presented here provide further insight into the complexity of flow in partially saturated heterogeneous formations, and may serve for the subsequent development of field-scale, vadose-zone transport models for complex real-world scenarios.

2. Transport of Reactive Solutes in Partially Saturated Heterogeneous Porous Formations

2.1 Outline of the Theoretical Framework

Transport of reactive solutes through partially saturated, heterogeneous formation in the case of a steady-state velocity field and chemical equilibrium is cast here in a Lagrangian framework, introducing the Eulerian retarded velocity field [Bellin et al., 1993], $u^R(\underline{x};\Theta) = u(\underline{x};\Theta)/r(\underline{x};\Theta)$. Here $u(\underline{x};\Theta)$ is the Eulerian velocity, $r(\underline{x};\Theta) = 1 + \rho_b(\underline{x})K_d(\underline{x})/n(\underline{x})\Theta(\underline{x})$ is the retardation factor, $K_d(\underline{x})$ is the solid-liquid partition coefficient, $\underline{x} = (x_1, x_2, x_3)$ is the spatial coordinate vector (with x_1 directed vertically downwards), Θ is water saturation, n is porosity and ρ_b is bulk density.

First-order approximations of the time-dependent displacement covariance tensor of the reactive solute, X^R_{ij} ($i, j = 1, 2, 3$), as a function of mean water saturation, are obtained by a two-stage approach. This approach combines a general Lagrangian description of the motion of an indivisible particle of a reactive solute by steady-state flow [Bellin et al., 1993] with a stochastic continuum description [Yeh et al., 1985a,b] of the steady-state flow in partially saturated, heterogeneous formations.

The first stage involves relating the statistical moments of the probability density function (PDF) of the particle displacement to those of the retarded-velocity PDF. The following assumptions are employed in this stage: (i) Lagrangian and Eulerian stationarity and homogeneity of the velocity field; (ii) given statistics of the velocity field; (iii) small fluctuations of particle displacement about the mean trajectory; (iv) large Péclet numbers; and (v) a linear, reversible, equilibrium-type reaction of the solute with the formation.

For ergodic conditions, neglecting pore-scale dispersion, and using a first-order approximation in the retarded velocity covariance, for a particle of a reactive solute injected into the flow field at time $t=0$ and location $\underline{x}=0$, the first two moments of the Lagrangian particle displacement, the mean, $\langle \underline{X}^R(t; \Theta) \rangle$ and, by a first-order approximation in the retarded velocity variance, the covariance tensor, $X_{ij}^R(t; \Theta) = \langle X_{i,j}^R(t; \Theta) X_{i,j}^R(t; \Theta) \rangle$, ($i, j=1, 2, 3$), at time t , and water saturation, Θ , where $\underline{X}^R = \underline{X}^R - \langle \underline{X}^R \rangle$ is the fluctuation, are given similar to Bellin et al. [1993] as

$$\langle \underline{X}^R(t; \Theta) \rangle = \underline{U}^R(\Theta) t \quad (2.1a)$$

and

$$X_{ij}^R(t; \Theta) = 2 \int_0^t (t - \tau) u_{ij}^R [\langle \underline{X}^R(\tau; \Theta) \rangle] d\tau \quad (2.1b)$$

where $\underline{U}^R = \underline{U}/R$ is the mean retarded Eulerian velocity vector, $\underline{U} = (U_1, U_2, U_3)$ is the mean Eulerian velocity vector, $R = \langle r(\underline{x}) \rangle$ is the mean retardation factor, and u_{ij}^R ($i, j=1, 2, 3$) is the retarded velocity covariance tensor. For saturated flow, a first-order approximation of u_{ij}^R for the physically plausible situation in which the retardation factor is correlated with log-saturated conductivity, $\log K_s$, and for the general case in which both $U_i \neq 0$ ($i=1, 2, 3$) and the mean head-gradient vector, $J_i \neq 0$ ($i=1, 2, 3$) was given by Bellin et al. [1993]. This approximation is adopted here for unsaturated flow, assuming that the retardation factor is correlated with log-unsaturated conductivity, $\log K$, i.e.,

$$u_{ij}^R(\xi; \Theta) = \frac{U_i U_j}{R(\Theta)^4} C_{rr}(\xi; \Theta) - \frac{U_i U_j}{R(\Theta)^3} \left[2 C_{ry}(\xi; \Theta) - \frac{1}{J_i} \frac{\partial C_{rh}(\xi; \Theta)}{\partial \xi_i} + \frac{1}{J_j} \frac{\partial C_{rh}(-\xi; \Theta)}{\partial \xi_j} \right] + \frac{u_{ij}(\xi; \Theta)}{R(\Theta)^2} \quad (2.2)$$

where $C_{rr}(\xi; \Theta)$ is the covariance of the perturbations of r , $C_{ry}(\xi; \Theta)$ and $C_{rh}(\xi; \Theta)$ are cross-covariances between the perturbations of r and $\log K$, and r and the capillary pressure head

ψ , respectively, $u_{ij}(\xi; \Theta)(i,j=1,2,3)$ is the Eulerian velocity covariance tensor and $\xi = \underline{x} - \underline{x}'$ is the separation vector.

The second stage involves relating the statistical moments of the PDF of the Eulerian velocity to those of the properties of the heterogeneous porous formation. The following assumptions are employed in this stage: (i) the local steady-state unsaturated flow obeys Darcy's law and continuity; (ii) the local relationships between unsaturated conductivity, K and the capillary pressure head, ψ are isotropic, as described by the Gardner [1958] model ((1.2)); (iii) both formation properties, $\log K_s$ and α , are multivariate normal (MVN) random space functions (RSF), ergodic over the region of interest, characterized at second order by constant means, $F = E[\log K_s]$ and $A = E[\alpha]$, and by statistically anisotropic exponential covariance functions, $C_{ff}(\xi)$ and $C_{aa}(\xi)$, respectively, given by (1.4); and (iv) the porosity, n , and for a given mean capillary pressure head, $H = \langle \psi(\underline{x}) \rangle$, water saturation, Θ is a deterministic constant, given [Russo, 1988] as:

$$\Theta(H) = [\exp(-\frac{1}{2}AH)(1 + \frac{1}{2}AH)]^{2/(m+2)} \quad (2.3)$$

where $m > -2$, is a parameter that accounts for the dependence of tortuosity and correlation between pores at two different cross sections of the porous formation, on water saturation. Note that the last assumption is justified in view of the relatively small variability in water saturation as compared with the variability in unsaturated conductivity, [Russo et al., 1994a].

Use of the aforementioned assumptions under ergodic conditions, and linearization of Darcy's law for unsaturated flow and for a given water saturation, Θ , results in a first-order approximation of the velocity covariance tensor, $u_{ij}(\xi; \Theta)(i,j=1,2,3)$

$$u_{ij}(\xi; \Theta) = \left[\frac{K_g(\Theta)}{n\Theta} \right]^2 \left[J_i J_j C_{yy}(\xi; \Theta) - J_i \frac{\partial C_{yh}(-\xi; \Theta)}{\partial \xi_j} + J_j \frac{\partial C_{yh}(\xi; \Theta)}{\partial \xi_i} + \frac{\partial^2 C_{hh}(\xi; \Theta)}{\partial \xi_i \partial \xi_j} \right] \quad (2.4)$$

where $K_g(\Theta)$ is the geometric mean unsaturated conductivity, $C_{yy}(\xi; \Theta)$ and $C_{hh}(\xi; \Theta)$ are the covariances of the perturbations of the log-unsaturated conductivity, $y = \log K$ and of the capillary pressure head, ψ , respectively, and $C_{yh}(\xi; \Theta)$ is the cross-covariance between perturbations of $\log K$ and ψ . Explicit expressions for the dependence of $C_{hh}(\xi; \Theta)$, $C_{yy}(\xi; \Theta)$ and $C_{yh}(\xi; \Theta)$ on the statistics of the formation properties and on mean saturation are given elsewhere [Yeh et al., 1985a,b; Russo, 1993; 1995b,c].

2.2 The Retarded Velocity

A heterogeneous porous formations of axisymmetric anisotropy (i.e., $I_{p2} = I_{p3} = I_{ph}$, $I_{p1} = I_{pv}$) with mean flow in the vertical direction, perpendicular to the formation bedding, i.e., $\mathbf{J} = (J_1, 0, 0)$ is considered here. Expressions for the dependence of the velocity covariance tensor (6) on the statistics of the formation properties and on mean saturation have been obtained for the general case in which the separation vector does not coincide with the mean gradient vector; these expressions are given in Chapter 1 and in Appendix A.

Evaluation of the retarded velocity covariance tensor (2.2) requires a few simplifying assumptions regarding the covariance, $C_{rr}(\xi; \Theta)$ and the cross-covariances, $C_{ry}(\xi; \Theta)$ and $C_{rh}(\xi; \Theta)$. Considering ρ_b as a deterministic constant, and the log-partition coefficient, $w = \log K_d(\mathbf{x})$ as a multivariate normal RSF, ergodic over the region of interest, characterized at second order by a constant mean and a statistically anisotropic exponential covariance function, the covariance of the retardation factor, $C_{rr}(\xi; \Theta)$, is given by (1.4) with $p=r$, where $\sigma_r^2 = (\rho_b K_d / n\Theta)^2 \exp(\sigma_w^2) [\exp(\sigma_w^2) - 1]$ is the variance of the retardation factor, r ,

$K_d^g = \exp(-\mu_w)$ is the geometric mean of K_d , μ_w and σ_w^2 are parameters of the distribution of $w = \log K_d$, and $I_r = (I_{r1}, I_{r2}, I_{r3})$ is the correlation scale of r . In this case, the cross-covariance between fluctuations of the retardation factor and of the log-unsaturated conductivity, $C_{ry}(\xi; \Theta)$ is also given by (1.4), with $p = ry$, where $\sigma_{ry}^2 = \rho_{ry} \sqrt{(\sigma_r^2 \sigma_y^2)}$ and ρ_{ry} are the cross-variance and the cross-correlation coefficient between perturbations of r and $\log K$, respectively, $I_{ry} = 2I_r I_y / (I_r + I_y)$, and $\sigma_y^2(\Theta)$ and $I_y(\Theta)$ are given [Russo, 1995b] as:

$$\sigma_y^2(\Theta) = \sigma_f^2 + H^2(\Theta) \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2 \quad (2.5a)$$

$$I_y(\Theta) = \frac{\sigma_f^2 I_f + H^2(\Theta) \sigma_a^2 I_a - 2H(\Theta) \sigma_{fa}^2 I_{fa}}{\sigma_f^2 + H^2(\Theta) \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2} \quad (2.5b)$$

where σ_{fa}^2 is the cross-variance between perturbation of $\log K_s$ and α , and $I_{fa} = 2I_f I_a / (I_f + I_a)$.

Following Bellin et al. [1993] we may express the cross-covariance between fluctuations of the retardation factor and the capillary pressure head gradient on the right-hand side (RHS) of (2.2) as:

$$-\frac{1}{J_i} \frac{\partial C_{rh}(\xi; \Theta)}{\partial \xi_i} + \frac{1}{J_j} \frac{\partial C_{rh}(-\xi; \Theta)}{\partial \xi_j} = C_{ry}(\xi; \Theta) E'_{ij}(\xi) \quad (2.6)$$

where $E'_{ij}(\xi) = E_{ij}(\xi; \Theta) / \{J_i [C_{ff}(\xi) + H^2(\Theta) C_{aa}(\xi) - 2H(\Theta) C_{fa}(\xi)]\}$, $E_{ij}(\xi; \Theta) = -(1/J_i) \partial C_{yh}(\xi; \Theta) / \partial \xi_i + (1/J_j) \partial C_{yh}(-\xi; \Theta) / \partial \xi_j$ ($i, j = 1, 2, 3$), $C_{yh}(\xi; \Theta) = \langle y(\mathbf{x}; \Theta) h(\mathbf{x}'; \Theta) \rangle$ is the cross-covariance between perturbations of $\log K$ and the capillary pressure head and $C_{fa}(\xi)$ is the cross-covariance between perturbations of $\log K_s$ and α .

2.3 The E'_{ij} Terms

The $E_{ij}(\xi; \Theta)$ ($i, j = 1, 2, 3$) terms are evaluated by using spectral representation techniques

[e.g., Yeh et al., 1985a,b; Russo, 1993, 1995b,c]. Without loss of generality, the case where the mean gradient is directed along the vertical axis (i.e., $\underline{J}=(J_1,0,0)$) is considered here. Furthermore, in the reminder of this chapter, $J_1=-\partial(-H-x_1)/\partial x_1$ is taken as unity, i.e., the mean flow is gravity-dominated. For heterogeneous porous formations of axisymmetric anisotropy, assuming that the correlation scales of $\log K_s$ and α are identical, i.e., $I_y=I_f=I_a$, the $E_{ij}(\xi;\Theta)$ ($i,j=1,2,3$) terms are given by (B3) in Appendix B. In particular, for $\xi=0$, the only nonzero component of $E'_{ij}(0)$, $E'_{11}(0)=E_{11}(0;\Theta)/\{J_1[\sigma_f^2+H^2(\Theta)\sigma_a^2-2H(\Theta)\sigma_{fa}^2]\}$, is given by:

$$E'_{11}(0) = -2 \int_{-1}^{+1} \frac{p^2 e^{-2} \{ (1-p^2+p^2 e^{-2})^3 - 3p^2 e^{-4} g^2 (1-p^2+p^2 e^{-2}) + 2p^3 e^{-6} g^3 \}}{[p^2 e^{-4} g^2 - (1-p^2+p^2 e^{-2})^2]^2} dp \quad (2.7a)$$

where $e=I_{yv}/I_{yh}$ is the anisotropy ratio, $I_{yv}=I_{y1}$, $I_{yh}=I_{y2}=I_{y3}$, and $g=(2J_1-1)AI_{yv}$.

The nondimensional $E'_{11}(0)$ term which is independent of Θ , is depicted in Fig. 2.1 as a function of the product AI_{yv} , for selected values of e . For the case of vertical mean flow, e is the ratio between scales of the formation heterogeneity in the direction of the mean flow, and in a direction normal to the mean flow. For fixed I_{yv} , decreasing e expresses a larger extent of the typical flow barriers in a direction normal to the mean flow. The converse is true for horizontal mean flow. The product AI_{yv} applies to unsaturated flow only. It can be interpreted as a length scale ratio, where I_{yv} is a characteristic length scale of heterogeneity in the direction of the mean flow, while $\lambda=A^{-1}$, the macroscopic capillary length scale, is a characteristic length scale of the unsaturated flow [Raats, 1976]. For fixed I_{yv} , the increase in $A=\langle\alpha\rangle$ expresses a transition from a fine-textured soil material, associated with significant capillary forces to a coarse-textured soil material, associated with negligible capillary forces [Russo, 1995b]. In the small limit of A , $A\rightarrow 0$, $E_{ij}(\xi;\Theta)$ ((B3)) (with $\Theta=1$, and $H=0$), reduces to its counterpart for saturated flow (for the case in which the mean flow

is perpendicular to the bedding).

For a given AI_{yv} , $E'_{11}(0)$ is largest at the small e limit, $e \rightarrow 0$ (a perfectly stratified formation with heterogeneity in the vertical direction only) and decreases with increasing e , approaching zero as $e \rightarrow \infty$ (heterogeneity in the horizontal direction only). At $e \rightarrow 0$, $E'_{11}(0)$ is given [Yeh et al., 1985b] by $E'_{11}(0) = -2/(1+g)$, which, in turn, degenerates to $E'_{11}(0) = -2$ at the small limit of A , $A \rightarrow 0$. For an isotropic formation ($e=1$), (2.7a) is integrated analytically [Yeh et al., 1985a] with the result

$$E'_{11}(0) = 2 \left[\frac{2}{g^2} \left[1 - \frac{2 \log |1+g|}{g} + \frac{1}{1+g} \right] - \frac{1}{1+g} \right] \quad (2.7b)$$

which, in turn, degenerates to $E'_{11}(0) = -2/3$ at the small limit of A , $A \rightarrow 0$, and is identical to its counterpart for flow in three-dimensional, isotropic aquifers [e.g., Bellin et al., 1993]. Note that for fixed I_{yv} , at the small limit of A , $A \rightarrow 0$, (2.7a) is integrated analytically with the result:

$$E'_{11}(0) = - \frac{2e^{-2} [-1 + e^{-2} + \sqrt{(1-e^{-2})} \tanh^{-1}(\sqrt{1-e^{-2}})]}{(-1 + e^{-2})^2} \quad (2.7c)$$

Fig. 2.2 depicts the normalized form, $E'_{11}(\xi)/E'_{11}(0)$ for selected values of AI_{yv} and the anisotropy ratio, $e = I_{yv}/I_{yh}$, demonstrating that for given water saturation and fixed I_{yv} , the persistence of E'_{11} increases with decreasing e and A . In other words, for fixed I_{yv} , the enhanced magnitude and persistence of the cross-correlation between perturbations of $\log K$ and the capillary pressure gradient, $\partial h / \partial x_1$, due to an increase in $I_{yh} = I_{yv}/e$, (i.e., an increase in the size of a typical flow barrier in a direction normal to the mean flow), is balanced by a decrease in the capillary forces (i.e., increasing A).

2.4 The Retarded Velocity Covariance

The nondimensional retarded velocity covariance, $u'^R_{11}(\xi; \Theta) = u'^R_{11}(\xi; \Theta) R^2(\Theta) / \sigma_y^2(\Theta) U^2$, is obtained by substituting (2.6) in (2.2), i.e.,

$$u'^R_{11}(\xi; \Theta) = \frac{1}{\sigma_y^2(\Theta)} \left[\frac{C_{rr}(\xi; \Theta)}{R^2(\Theta)} - [2 + E'_{11}(\xi)] \frac{C_{ry}(\xi; \Theta)}{R(\Theta)} + \frac{u_{11}(\xi; \Theta)}{U^2} \right] \quad (2.8)$$

Note that unlike the nondimensional velocity covariance, $u'_{11}(\xi) = u_{11}(\xi; \Theta) / \sigma_y^2(\Theta) U^2$, which is independent of Θ , (Russo, 1995b,c), $u'^R_{11}(\xi; \Theta)$ ((2.8)) depends on Θ . This stems from the dependence of the retardation factor, r , the cross-covariance C_{ry} , and the covariance C_{rr} on Θ . Consequently, the division of the RHS of (2.8) by $\sigma_y^2(\Theta)$ does not cancel the effect of Θ on the first two terms on the RHS of (2.8).

The first term on the RHS of (2.8) depends only on the chemical heterogeneity of the formation while the third term on the RHS of (2.8) depends only on the physical heterogeneity of the formation. The second term on the RHS of (2.8) represents interaction between the effects of the chemical and physical heterogeneities on the retarded velocity. It is clear from (2.8) that the effect of $e = I_{yv} / I_{yh}$ and AI_{yv} on $u'^R_{11}(\xi; \Theta)$ is a direct consequence of their effect on the two last terms on the RHS of (2.8). For a given Θ and given statistics of the retardation factor field and its cross-correlation with the log-conductivity field, therefore, the nondimensional retarded velocity variance, $u'^R_{11}(0; \Theta)$, (given by (10) for $\xi = 0$) increases (for $\sigma_{ry}^2 < 0$) or decreases (for $\sigma_{ry}^2 > 0$) with increasing e and decreasing AI_{yv} . For the small A limit, $A \rightarrow 0$, a closed-form analytical expression can be obtained for $u'^R_{11}(0; \Theta)$, using (2.7c) for $E'_{11}(0)$ and (16a) of Russo [1995a] for $u'_{11}(0)$. In this case (for given $\sigma_r^2(\Theta)$ and $\sigma_{ry}^2(\Theta) < 0$), $u'^R_{11}(0; \Theta)$ is a monotonic increasing function of e . At the small e limit, $e \rightarrow 0$, $E'_{11}(0) \rightarrow -2$ and $u'_{11}(0) \rightarrow 0$, hence $u'^R_{11}(0; \Theta) \rightarrow$

$\sigma_r^2(\Theta)/\sigma_y^2(\Theta)R^2(\Theta)$. On the other hand, at the large e limit, $e \rightarrow \infty$, $E'_{11}(0) \rightarrow 0$, and $u'_{11}(0) \rightarrow 1$, hence $u'^R_{11}(0; \Theta) \rightarrow 1 + [\sigma_r^2(\Theta)/R^2(\Theta) - 2\sigma_{ry}^2(\Theta)/R(\Theta)]/\sigma_y^2(\Theta)$. For the isotropic case ($e=1$), $E'_{11}(0) = -2/3$ and $u'_{11}(0) = 8/15$, hence $u'^R_{11}(0; \Theta) = 8/15 + [\sigma_r^2(\Theta)/R^2(\Theta) - (4/3)\sigma_{ry}^2(\Theta)/R(\Theta)]/\sigma_y^2(\Theta)$, which is identical to its counterpart for saturated flow in three-dimensional, isotropic aquifers [Bellin et al., 1993]. In other words, the relative impact of the chemical heterogeneity of the formation on $u'^R_{11}(0; \Theta)$ increases with decreasing e . For a perfectly stratified formation, ($e \rightarrow 0$), $u'^R_{11}(0; \Theta)$ depends only on the chemical heterogeneity of the formation.

It is clear ((2.8)) that the sign of $\sigma_{ry}^2(\Theta)$ has a considerable impact on $u'^R_{11}(0; \Theta)$. In line with the findings of Robin et al. [1991] for transport of sorptive solutes under saturated flow which suggest a negative cross-correlation between the retardation factor, r and $\log K_s$, the physically plausible situation in which r is negatively correlated with $\log K$ ($\sigma_{ry}^2 < 0$) is assumed in the present chapter. Fig. 2.3 depicts the ratio between the retarded velocity variance, $u'^R_{11}(0; \Theta)$ and the velocity variance, $u'_{11}(0)$ for selected values of AI_{yv} and the anisotropy ratio, $e = I_{yv}/I_{yh}$. Results which are presented in Fig. 2.3 and in the reminder of the present chapter are calculated using the following constants: $n=0.4$, $\Theta=0.95$, $K_g=0.38\text{m/d}$ (i.e., $U=1\text{m/d}$), $\rho_b=1.2\text{Mg/m}^3$ and $K_d^g=0.625\text{m}^3/\text{Mg}$, (i.e., $R \approx 3$) and statistical parameters, $\sigma_f^2=0.875$, $CV_a = \sqrt{\sigma_a^2}/A=0.5$, $\rho_{fa}=0$, (i.e., $\sigma_y^2=1$), $I_{yv}=0.25\text{m}$, $CV_r = \sqrt{\sigma_r^2}/R=0.5$, and $\rho_{ry}=-0.5$.

For a given Θ , $u'_{11}(0; \Theta)$ decreases with decreasing e and increasing A (see Chapter 1), while $E'_{11}(0)$ increases (Fig. 2.2) with decreasing e and decreasing A . Furthermore, for a given e , the rate at which $u'_{11}(0; \Theta)$ decreases with increasing A is faster than the rate at which $E'_{11}(0)$ decreases with increasing A . Consequently, the ratio $u'^R_{11}(0; \Theta)/u'_{11}(0)$ increases (for $\sigma_{ry}^2 < 0$, Fig. 2.3) or decreases (for $\sigma_{ry}^2 > 0$) with decreasing e and increasing

A. Fig. 2.4 depicts the normalized velocity covariance, $u'_{11}(\xi)/u'_{11}(0)$ and the normalized retarded velocity covariance, $u'^R_{11}(\xi;\Theta)/u'^R_{11}(0;\Theta)$ for selected values of AI_{yv} and e , demonstrating that for a given AI_{yv} , the persistence of both u'_{11} and u'^R_{11} increases with decreasing e . For a given e , however, although for relatively small scaled separation distances, ξ , both u'_{11} and u'^R_{11} increases with decreasing AI_{yv} , their persistence increases with increasing AI_{yv} . This means that the effect of e and AI_{yv} on the ratio $u'^R_{11}(\xi;\Theta)/u'_{11}(\xi;\Theta)$ at the small ξ limit, $\xi=0$ (Fig. 2.3) persists for $\xi > 0$. However, for ξ larger than few log-conductivity correlation scales, and given e , the ratio $u'^R_{11}(\xi;\Theta)/u'_{11}(\xi;\Theta)$ decreases with increasing AI_{yv} . Figs. 2.3 and 2.4 demonstrate that for fixed I_{yv} , the relative impact of the chemical heterogeneity of the formation on the variability of the flow increases with increasing A (soil material of coarser texture) and decreasing e (larger extent of the typical flow barriers in a direction normal to the mean flow). This is due to the fact that when the mean flow is vertical, large A and small e both reduce the impact of the heterogeneity in the physical properties of the formation on the variability of the flow in the longitudinal direction (see Chapter 1).

2.5 Reactive Transport

The displacement covariance tensor for a reactive solute, $X^R_{ij}(t;\Theta)$ ($i,j=1,2,3$) is calculated by substitution of (2.1a) and (2.2) in (2.1b) and integrating along a line parallel to the mean gradient of unit vector $\underline{U}^R/|\underline{U}^R|$. Assuming that the correlation scales of $\log K_s$, α and r are identical, *i.e.*, $I_r = I_y$, X^R_{ij} ($i,j=1,2,3$) is given by

$$X_{ij}^R(t';\Theta) = \frac{2 U_i U_j I_{yv}^2}{U^2} \left[\frac{\sigma_r^2(\Theta) [1 - \exp(t') + t' \exp(t')]}{R(\Theta)^2 \exp(t')} \right. \\ \left. - \frac{\sigma_{ry}^2(\Theta)}{R(\Theta) \exp(t')} \{ 2 [1 - \exp(t') + t' \exp(t')] + \exp(t') G'_{ij}(t') \} \right] + X_{ij}(t';\Theta) \quad (2.9)$$

where $t' = t|U|/I_{yv}R$, $X_{ij}(t';\Theta)$ ($i,j=1,2,3$) is the respective displacement covariance tensor for tracer solute (given by (1.19)), and the tensor $G'_{ij}(t')$ ($i,j=1,2,3$) is given by (C2) in Appendix C; both are functions of e and A . Similarly, the macrodispersion tensor for a reactive solute, $D_{ij}^R(t';\Theta) = (1/2)dX_{ij}^R(t';\Theta)/dt'$, ($i,j=1,2,3$) is given by

$$D_{ij}^R(t';\Theta) = \frac{U_i U_j I_{yv}}{UR(\Theta)} \left[\frac{\sigma_r^2(\Theta) [\exp(t') - 1]}{R(\Theta)^2 \exp(t')} \right. \\ \left. - \frac{\sigma_{ry}^2(\Theta)}{R(\Theta) \exp(t')} \{ 2 [\exp(t') - 1] + \exp(t') G''_{ij}(t') \} \right] + \frac{D_{ij}(t';\Theta)}{R(\Theta)} \quad (2.10)$$

where $D_{ij}(t';\Theta)$ ($i,j=1,2,3$) is the respective macrodispersion tensor for tracer solute (given by (1.20)) and $G''_{ij}(t')$ ($i,j=1,2,3$) is given by (C5) in Appendix C; both are functions of e and A .

It is clear ((2.1b)) that the behavior of $X_{11}^R(t';\Theta)$ ((2.9)), and, concurrently, of $D_{11}^R(t';\Theta)$ ((2.10)) is related to the behavior of the retarded velocity covariance, $u_{11}^R(\xi;\Theta)$ ((2.8)). As in the case of (2.8), the first term on the RHS of (2.9) depends only on the chemical heterogeneity of the formation while the third term on the RHS of (2.9) depends only on the physical heterogeneity of the formation. The second term on the RHS of (2.9) represents interaction between the effects of the chemical and physical heterogeneities on the transport of the reactive solute. The same is true for $D_{ij}^R(t',\Theta)$ ((2.10)). It is clear from (2.9) and (2.10) that the effect of $e=I_{yv}/I_{yh}$ and AI_{yv} on $X_{11}^R(t';\Theta)$ and $D_{11}^R(t',\Theta)$ is a direct

consequence of their effect on $G'_{11}(t')$ and $X_{11}(t';\Theta)$, and $G''_{11}(t')$ and $D_{11}(t';\Theta)$, respectively.

Dimensionless forms of the longitudinal components of (2.10), *i.e.*, $D'^R_{11}(t';\Theta) = D^R_{11}(t';\Theta)R(\Theta)/\sigma_y^2(\Theta)I_{yv}U$, are presented as functions of the dimensionless travel time, $t' = tU/RI_{yv}$ in Fig. 2.5, for selected values of e and AI_{yv} . For given Θ , e and AI_{yv} , the time behavior of D'^R_{11} is similar to its counterpart for tracer solute. This stems from the fact that both $X'_{11} = X_{11}/\sigma_y^2(\Theta)I_{yv}^2$ and $X'^R_{11} = X^R_{11}/\sigma_y^2(\Theta)I_{yv}^2$ increase with travel time faster than linearly in t' as the solute first invades the flow system, and tend to evolve at a linear rate. For $\rho_{ry} < 0$, however, the evolution of X'^R_{11} at a rate faster than linearly in t' persists longer than X'_{11} . In other words, D'^R_{11} approaches its asymptotic value at a slower rate than D'_{11} (Fig. 2.5), while the opposite is true for $\rho_{ry} > 0$. Note that unlike their counterparts for tracer solute, $X'_{11} = X_{11}/\sigma_y^2(\Theta)I_{yv}^2$ and $D'_{11} = D_{11}/\sigma_y^2(\Theta)I_{yv}U$, respectively, which are independent of Θ , [Russo, 1995b,c] both X'^R_{11} and D'^R_{11} depend on Θ . As in the case of u'^R_{11} , this stems from the dependence of the retardation factor, r , the cross-variance, σ_{ry}^2 and the variance, σ_r^2 on Θ .

The effect of $e = I_{yv}/I_{yh}$ and AI_{yv} on $X'^R_{11}(t';\Theta)$ ((2.9)) and $D'^R_{11}(t',\Theta)$ ((2.10)) (Fig. 2.5) is a direct consequence of their effect on $G'_{11}(t')$ and $X_{11}(t';\Theta)$, and $G''_{11}(t')$ and $D_{11}(t';\Theta)$, respectively, which, in turn, depend on $u'_{11}(\xi)$ and $E'_{11}(\xi)$. The dependence of $u'_{11}(\xi)$ and $E'_{11}(\xi)$ on e and AI_{yv} was discussed in the previous sections, *i.e.*, $u'_{11}(\xi)$ increases with increasing e and decreasing AI_{yv} , while $E'_{11}(\xi)$ decreases with increasing e and increasing AI_{yv} . Furthermore, for a given e , the rate at which $u'_{11}(\xi)$ increases with decreasing AI_{yv} is faster than the rate at which $E'_{11}(\xi)$ decreases with increasing AI_{yv} . Consequently, for a given Θ and $\sigma_{ry}^2 < 0$, both $X'^R_{11}(t';\Theta)$ and $D'^R_{11}(t',\Theta)$ (Fig. 2.5) increase with increasing e and decreasing AI_{yv} . In other words, enhanced spreading of both

reactive and tracer solutes in the longitudinal direction is expected particularly in formations with typical flow barriers which are small in a direction perpendicular to the mean flow, relative to their size in the direction parallel to the mean flow (large aspect ratio, $e=I_{yv}/I_{yh}$), and in formations of fine-textured soil material with significant capillary forces (small A).

Focusing on the relative impacts of the physical and the chemical heterogeneities of the formation on the spreading of reactive solutes and using the aforementioned findings, it can be shown that for given Θ and $\sigma_{ry}^2 < 0$, the first and the second terms on the RHS of (2.9) which represent effects of the chemical heterogeneity, and the interaction between the effects of the chemical and physical heterogeneities, respectively, on the transport, mitigate the rate at which $X_{11}^R(t';\Theta)$ decreases with decreasing e and increasing AI_{yv} . Consequently, $X_{11}^R(t';\Theta)$ decreases with decreasing e and increasing AI_{yv} at a rate slower than its counterpart for tracer solute, $X_{11}(t';\Theta)$. The same is true for (2.10). In other words, larger impact of the chemical heterogeneity of the formation on the spreading of reactive solutes in the longitudinal direction, (*i.e.*, larger ratios of $X_{R11}(t';\Theta)/X_{11}(t';\Theta)$ and $D_{R11}(t';\Theta)/D_{11}(t';\Theta)$) are expected in formations of coarse-textured soil materials (large A) and in formations which exhibit a significant stratification (small e).

The longitudinal component of the asymptotic, constant, macrodispersion tensor for reactive solute, D_{11}^R , is calculated from (2.10). For $i=j=1$ and $t \rightarrow \infty$, $G''_{11} \rightarrow 0$, and (2.10) reduces to

$$D_{11}^R(\Theta) = \frac{UI_{yv}}{R(\Theta)} \left[\frac{\sigma_r^2(\Theta)}{R(\Theta)^2} - \frac{2\sigma_{ry}^2(\Theta)}{R(\Theta)} + \sigma_y^2(\Theta) \right] \quad (2.11)$$

which, in turn, is identical to its counterpart for flow in three-dimensional, isotropic aquifers [Bellin et al., 1993]. Note that for a given Θ , like its counterpart for tracer solute, $D'_{11} = D_{11}/\sigma_y^2(\Theta)I_{yv}U$ which is a constant ($D'_{11}=1$), irrespective of the values of e and

AI_{yv} , the asymptotic $D'^R_{11} = 1 + \{[\sigma_r^2(\Theta) - 2R(\Theta)\sigma_{ry}^2(\Theta)]/R^2(\Theta)\sigma_y^2(\Theta)\}$ is also independent of e and AI_{yv} . However, unlike the asymptotic D'_{11} , which is independent of water saturation, Θ , the asymptotic D'^R_{11} depends on Θ .

2.6 Effect of Mean Water Saturation

The effect of mean water saturation on the velocity covariance tensor, $u_{ij}(\xi, \Theta)$, the displacement covariance tensor, $X_{ij}(t, \Theta)$ and the macrodispersion tensor, $D_{ij}(t, \Theta)$ for tracer solutes is due to its effects on the variance, $\sigma_y^2(\Theta)$ and correlation scale, $I_y(\Theta)$ ((2.5)) [Russo, 1995b,c]. A detailed analysis of the dependence of $\sigma_y^2(\Theta)$ and I_y on water saturation and on the statistics of the $\log K_s$ and the α fields and the cross-correlation between the two fields is given elsewhere [Russo, 1995b]. Note that in the present study, due to the assumption of $I_a = I_f$, I_y is independent of Θ . As for $\sigma_y^2(\Theta)$, the results of the analysis of Russo [1995b] reveal that for $\rho_{fa} \leq 0$, $\sigma_y^2(\Theta)$ is a monotonically decreasing function of Θ , while for $\rho_{fa} > 0$, $\sigma_y^2(\Theta)$ is a nonmonotonic function of Θ , increasing with decreasing Θ when $\Theta < \Theta_c(H_c)$, where H_c is given [Russo, 1995b] by $H_c = \rho_{fa} \sqrt{(\sigma_a^2/\sigma_f^2)}$. Consequently, $u_{ij}(\xi, \Theta)$, $X_{ij}(t, \Theta)$ and $D_{ij}(t, \Theta)$ increase with decreasing Θ , (for the entire range of Θ , when $\rho_{fa} \leq 0$, and for $\Theta < \Theta_c$, when $\rho_{fa} > 0$).

In the case of reactive solutes, $u^R_{ij}(\xi, \Theta)$, $X^R_{ij}(t, \Theta)$ and $D^R_{ij}(t, \Theta)$ are affected by $\sigma_y^2(\Theta)$ similarly to their counterparts for tracer solute, as well as by $\sigma_r^2(\Theta)/R^2(\Theta)$ and $\sigma_{ry}^2(\Theta)/R(\Theta)$ that, in turn, decrease with increasing Θ , and thus contribute to the increase in $u^R_{ij}(\xi, \Theta)$, $X^R_{ij}(t, \Theta)$ and $D^R_{ij}(t, \Theta)$ with decreasing water saturation. Note, however, that because $\sigma_y^2(\Theta)$ increases with decreasing Θ faster than $[\sigma_r^2(\Theta)/R^2(\Theta) - 2\sigma_{ry}^2(\Theta)/R(\Theta)]$ ((2.11)), the ratio $D^R_{11}(\Theta)/D_{11}(\Theta)$ decreases with decreasing Θ , (for the entire range of Θ , when $\rho_{fa} \leq 0$, and for $\Theta < \Theta_c$, when $\rho_{fa} > 0$, Fig. 2.6).

2.7 Concluding Remarks

First-order analysis, based on a stochastic continuum presentation of the Eulerian retarded velocity in a heterogeneous, partially saturated porous formation and a general Lagrangian description of the transport, were used to investigate the effect of both the anisotropy of the formation and the texture of the soil materials constituting the formation, on the spreading of reactive (sorptive) solutes under unsaturated flow. The physically plausible situation in which the retardation factor is negatively correlated with log-unsaturated conductivity was considered in this study. The case in which the mean gradient vector, $\underline{J}$, coincides with the principal axes of the formation heterogeneity was analyzed here. The analysis, however, can be extended to the general case in which $\underline{J}$ is inclined to the principal axes of the formation heterogeneity at arbitrary angles (Chapter 1).

Results of the analyses show that for a given water saturation and gravity-dominated unsaturated flow, both the physical and chemical heterogeneities of the formation enhance the spreading of the reactive solute in the longitudinal direction. This applies especially in formations with typical flow barriers which are small in a direction perpendicular to the mean flow, relative to their size in the direction parallel to the mean flow (large aspect ratio, $e = I_{yv}/I_{yh}$), and in formations of fine-textured soil materials with significant capillary forces (large macroscopic capillary length scale, $\lambda = A^{-1}$). The relative impact of the chemical heterogeneity of the formation on the spreading of the reactive solute, however, increases with decreasing λ and decreasing e . This result stems from the fact that when the mean flow is vertical, small λ and small e both diminish the impact of the heterogeneity in the physical properties of the formation on the variability of the flow in the longitudinal direction. The result that the relative impact of the chemical heterogeneity of the formation on the spreading of the reactive solute increases with decreasing e is in contrast with the result which is

expected for transport by horizontal mean flow in saturated formations (aquifers) for which $E'_{11}(\xi)$ decreases, while $u'_{11}(\xi)$ [Rubin and Dagan, 1992; Russo, 1995a] increases, with decreasing $e = I_{yv}/I_{yh}$.

Before concluding we would like to emphasize the limitations of this study. The retarded velocity covariance and displacement covariance tensors presented here were derived for an unbounded flow domain associated with a constant mean head gradient, $\underline{J}$. For bounded flow situations, such as a flow approaching a water table, in which $\underline{J}$ is not constant, however, the applicability of the results of this study would be restricted to situations in which $\underline{J}$ varies slowly over the log-conductivity correlation scale (i.e., in the range $AI_{yv} < \approx 0.1$).

Another limitation is due to the small-perturbations, first-order approximations of the retarded velocity covariance tensor and the Lagrangian displacement tensor. Consequently, the results are formally limited to formations with log-unsaturated conductivity variances smaller than unity. The simplifying assumptions regarding the local flow (steady-state flow), the local unsaturated conductivity ((1.2)), the uniform in space $\Theta(\psi)$ relationships ((2.3)), the type of the reaction of the solute with the formation (linear, reversible, equilibrium), the correlation scales (same for the physical and the chemical properties of the formation), and the relationships between the physical and the chemical properties of the heterogeneous formation (negative cross-correlation between the retardation factor and the log-unsaturated conductivity), might also limit the applicability of the results of this study. A rigorous analysis of these limitations, however, is beyond the scope of this investigation.

With these limitations in mind, we believe that the results presented in this chapter provide further insight into the complexity of flow and transport in partially saturated heterogeneous formations, and may serve for the subsequent development of tools for the analysis of field-scale, vadose-zone transport under realistic flow conditions.

3. Estimation of Parameters of Log-unsaturated Conductivity Covariance From Solute Transport Data

3.1 Mathematical Statement of the Problem

3.1.1 The Response of the Transport Domain

The movement of a pulse of a tracer solute in a partially saturated, heterogeneous, porous formation under steady-state, unidirectional vertical flow with water saturation, Θ is considered here. It is assumed that the length scales of both the flow domain and the nonuniformity of the average flow are much larger than that of the soil heterogeneity.

It is further assumed that measurements of the resident concentrations, c_r (defined as mass per unit volume of soil solution), at various elapsed times are available. Because of the complex heterogeneity of the formation hydraulic properties, however, the point values of c_r are subject to considerable uncertainty. Consequently, we focus our attention on larger-scale, integrated measures of the solute transport, such as the spatial moments of the distribution of the point values of c_r , since these moments are subject to a much lesser degree of uncertainty than are the point values.

For a finite body of a passive solute with initial condition $c_r(\underline{x}, t) = c_0$ in an initial injection planar area, A_0 which is orthogonal to the mean flow direction, and water saturation, Θ , the zeroth-moment of the spatial distribution of c_r is constant given by $M = \int n(\underline{x})\Theta(\underline{x})c_r(\underline{x}, t)d\underline{x} = n(\underline{x})\Theta(\underline{x})c_0A_0$, while its first and second moments are given [Dagan, 1989] as

$$\underline{R}(t) = \frac{1}{M} \int n(\underline{x})\Theta(\underline{x})c_r(\underline{x}, t)\underline{x}d\underline{x} \quad (3.1a)$$

$$S_{ij}(t) = \frac{1}{M} \int n(\underline{x})\Theta(\underline{x})[x_i - R_i(t)][x_j - R_j(t)]c_r(\underline{x}, t)d\underline{x} \quad (3.1b)$$

where M is the total injected mass of solute, n is the porosity, $\underline{R}(t)$ is the coordinate of the centroid of the solute plume, and $S_{ij}(t)$ ($i, j = 1, 2, 3$) are proportional to the moments of inertia of the plume.

3.1.2 The Forward Problem

The forward problem focuses on the prediction of the response of the transport domain, for given statistics of the relevant formation properties and given boundary and initial conditions. This task may be achieved by employing numerical methods, which combine a statistical generation method to produce realizations of the heterogeneous formation properties at sufficient resolution, with appropriate numerical methods to solve the partial differential equations governing flow and transport in unsaturated, heterogeneous formations. Such numerical methods [e.g., Russo et al., 1994a] are time consuming and computationally intensive, and thus highlight the need for simple, approximate solutions of the transport problem.

In the present Chapter we employ the simplified approach presented in Chapter 1, based on a general Lagrangian description of the transport [e.g., Dagan, 1984] and a stochastic continuum description of the unsaturated flow [Yeh et al., 1985a,b]. In this framework, the transport is described in terms of the motion of indivisible solute particles which are convected by the fluid. Neglecting pore-scale dispersion, the particle trajectory, $\underline{X}(t)$ is the solution of the kinematic equation $d\underline{X}/dt = \underline{V}(\underline{X})$, with $\underline{X} = \underline{a}$ for $t = 0$, where $\underline{V} = \underline{U} + \underline{u}$ is the Eulerian velocity, $\underline{U} = \langle \underline{V} \rangle$ is its expected value, assumed to be constant and uniform in time and space, and $\underline{u}$ is its fluctuation.

The first two statistical moments of $\underline{X}$ as functions of t and Θ and of the statistics of the formation properties are obtained by a two-stage approach. For the sake of completeness they

are briefly described here. The first stage involves relating the statistical moments of the PDF of the particle displacement to those of the velocity PDF. The following assumptions are employed in this stage: (i) Lagrangian and Eulerian stationarity and homogeneity; (ii) given statistics of the velocity field; (iii) small fluctuations of particle displacement about the mean trajectory; and (iv) large Péclet numbers.

Under the aforementioned assumptions and for ergodic conditions, for a particle of a solute injected into the flow field at time $t=0$ and fixed location $\underline{x}=\underline{a}$, the first two moments of $\underline{X}$, the particle displacement mean, $\langle \underline{X}(t;\Theta) \rangle$ and, by a first-order approximation in the velocity variance, the particle displacement covariance, $X_{ij}(t;\Theta) = \langle X'_i(t;\Theta)X'_j(t;\Theta) \rangle$, ($i,j=1,2,3$), at time t , and water saturation, Θ where $\underline{X}' = \underline{X} - \langle \underline{X} \rangle$ is the fluctuation, are given by (1.16).

Under ergodic conditions for the spatial moments ((3.1)), supposed to prevail if the characteristic length scale of the release zone is much larger than the heterogeneity scale in the transverse direction, $\underline{R}(t) \approx \langle \underline{R}(t) \rangle = \underline{U}t$ and $S_{ij}(t;\Theta) \approx \langle S_{ij}(t;\Theta) \rangle = S_{ij}(0;\Theta) + X_{ij}(t;\Theta)$ ($i,j=1,2,3$) [Dagan, 1989]. Hence, under ergodic conditions, the one-particle-trajectory statistical moments (1.16) characterize the spatial moments of the solute body ((3.1)).

The second stage involves relating the statistical moments of the PDF of the Eulerian velocity to those of the properties of the heterogeneous porous formation and is described in Chapter 2. Combining the two aforementioned stages, the displacement covariance tensor, $X_{ij}(t;\Theta)$ can be obtained by substituting the Fourier transform of the spectrum of (2.4) in (1.16b) (*i.e.*, (1.19). For x_1 directed vertically downwards, assuming axisymmetric anisotropy, (*i.e.*, $I_{pv}=I_{p1}$ and $I_{ph}=I_{p2}=I_{p3}$, $p=f,a$) for the case where $\underline{J}$ coincides with the longitudinal axis of the formation heterogeneity, assuming that the correlation scales of $\log K_s$ and α are identical, *i.e.*, $I_f=I_a$, first-order approximations of the principal components of

$X_{ij}(t; \Theta)$, $X_{ii}(t; \Theta)$ ($i=1$ to m), where $m=2$ or 3 , is the space dimension, are given by

$$X_{ii}(t; \Theta) = \frac{\sigma_w^2(\Theta) I_{wv}^2(\Theta)}{2\pi} \int_{-1}^{+1} \int_0^{2\pi} \frac{C_{mi} b_3 d\mu dr}{[(d_m^2 + r^2 e^{-2})^2 - r^2 e^{-4} g^2]^2} \quad (3.2a)$$

where $C_{m1} = \{(1-r^2)[\cos^2\mu + (m-2)\sin^2\mu]\}^2$, $C_{m2} = r^2 e^{-2}(1-r^2)\cos^2\mu$, $C_{m3} = (m-2)r^2 e^{-2}(1-r^2)\sin^2\mu$, $d_m = \sqrt{C_{m1}}$, $e = I_{yv}/I_{yh}$, $g = (2J_1 - 1)A I_{yv}$, b_3 is given by

$$b_3 = \frac{\exp(|r|t') (d_m^2 + r^2 e^{-2} - |r| e^{-2} g)^2 - (d_m^2 + r^2 e^{-2})^2 (1 + |r|t')}{r^2 \exp(|r|t')} \\ - \frac{r^2 e^{-4} g^2 (1 - |r|t')}{r^2 \exp(|r|t')} + \frac{2|r| e^{-2} g (d_m^2 + r^2 e^{-2})}{r^2 \exp[\frac{r^2 e^{-2} g t'}{d_m^2 + r^2 e^{-2}}]} \quad (3.2b)$$

$t' = Ut/I_{wv}(\Theta)$, $I_{wv}(\Theta) = I_{w1}(\Theta)$, $I_{yh}(\Theta) = I_{yi}(\Theta)$, $i=2$ to m , and $\sigma_w^2(\Theta)$ and $I_{wi}(\Theta)$ are given by (2.5) (with w replacing y).

Note that for $I_f = I_a$, $I_w = I_f = I_a$, independent of Θ , and that for $m=3$, because of the assumption of isotropy in the horizontal x_2x_3 plane, $X_{33}(t; \Theta) = X_{22}(t; \Theta)$. Furthermore, in this case, the C_{mi} ($i=1,2,3$) terms in (3.2a) are independent of μ ; thus, for $m=3$, calculation of $X_{ii}(t; \Theta)$ ($i=1$ to 3) requires integration of the RHS of (3.2a) with respect to r only. For both $m=2$ and $m=3$, $X_{ii}(t; \Theta)$ ($i=1$ to m) ((3.2)) are illustrated graphically elsewhere [Russo, 1997a] and are consistent with those derived for mean flow in the horizontal direction, parallel to the bedding of the saturated formation [Dagan, 1984, 1988]. For given Θ and J_1 , $X_{ii}(t; \Theta)$ ($i=1$ to m) ((3.2)) depends on four parameters characterizing the unsaturated, heterogeneous formation, i.e., σ_w^2 , I_{wv} , $e = I_{wv}/I_{wh}$, and $A = \langle \alpha(\underline{x}) \rangle$, which, in turn, can be used to characterize the log-unsaturated conductivity covariance (1.5).

3.1.3 Log-Unsaturated Conductivity Covariance

The log-unsaturated conductivity covariance (1.5) may be reduced to $C_{yy}(\xi; \Theta) = C_{ff}(\xi) + H^2(\Theta)C_{aa}(\xi) - A^2C_{hh}(\xi; \Theta)$. This stems from the equality $-A[C_{fh}(\xi; \Theta) + C_{fh}(-\xi; \Theta)] + AH(\Theta)[C_{ah}(\xi; \Theta) + C_{ah}(-\xi; \Theta)] = -2A^2C_{hh}(\xi; \Theta)$ [Russo, 1995b,c]. Furthermore, because of the dependence of $C_{yy}(\xi; \Theta)$ on $C_{hh}(\xi; \Theta)$, $C_{yy}(\xi; \Theta)$ is anisotropic even in isotropic formations. In the direction parallel to the mean flow, $C_{hh}(\xi; \Theta)$ is a "hole" function which exhibits negative values at moderate values of ξ_1 . Consequently, $C_{yy}(\xi_1, 0, 0; \Theta)$ is positive, having a correlation scale, $I_{y1}(\Theta)$ given by (3.3b) below. On the other hand, in the direction normal to the mean flow $C_{hh}(\xi; \Theta)$ is a positive function. Thus, $C_{yy}(0, \xi_2, 0; \Theta)$ and $C_{yy}(0, 0, \xi_3; \Theta)$ are "hole" functions, the correlation scales of which might be negative and, hence, physically meaningless.

The log-conductivity variance, $\sigma_y^2(\Theta)$ and its correlation scale in the longitudinal, vertical direction, $I_{yv}(\Theta) = I_{y1}(\Theta) = [1/\sigma_y^2(\Theta)]_0 \int^\infty C_{yy}(\xi_1, 0, 0; \Theta) d\xi_1$, are given as:

$$\sigma_y^2(\Theta) = \sigma_w^2(\Theta) - A^2\sigma_h^2(\Theta) \quad (3.3a)$$

$$I_{yv}(\Theta) = \frac{\sigma_w^2(\Theta)I_{wv}(\Theta) - A^2C_{hh}(\xi_1, 0, 0; \Theta)}{\sigma_w^2(\Theta) - A^2\sigma_h^2(\Theta)} \quad (3.3b)$$

where $\sigma_h^2(\Theta)$ is the variance of the perturbations of the capillary pressure head.

Note that since for given Θ and given statistics of the $\log K_s$ and the α fields, both $\sigma_h^2(\Theta)$ and $I_h(\Theta)$ depend on the anisotropic ratio, e and on $A = \langle \alpha(\underline{x}) \rangle$, $\sigma_y^2(\Theta)$ and $I_{yi}(\Theta)$ ($i=1$ to m) and, concurrently, the log-unsaturated conductivity covariance depends on both A and e . As was shown in Chapter 1, for given Θ and given statistics of the $\log K_s$ and the α fields, $\sigma_y^2(\Theta)$ decreases with increasing A and decreasing e , while the converse is true for $I_{yv}(\Theta)$. Note that as $A \rightarrow 0$, $\sigma_y^2(\Theta) \rightarrow \sigma_w^2(\Theta)$ and $I_y(\Theta) \rightarrow I_w(\Theta)$.

3.2.1 The Inverse Problem

For a given water saturation, Θ , our objective is to estimate the parameters of the log-unsaturated conductivity covariance, namely, $\sigma_y^2(\Theta)$ and $I_y(\Theta)$ (3.3), that, in turn, depend on four parameters: $\sigma_w^2(\Theta)$, $I_{ww}(\Theta)$, e and A . In the following sections we will investigate the feasibility of estimating these parameters from the response of the transport domain, expressed in terms of the principal components of the second spatial moments $S_{ij}(t; \Theta)$ ((3.1b)). The inverse problem is formulated here as a nonlinear optimization problem, i.e., the parameters $\sigma_w^2(\Theta)$, $I_{ww}(\Theta)$, e and A are estimated by minimizing a suitable objective function which expresses the discrepancy between observed and predicted system response. When measurement errors follow a multivariate normal distribution, with zero mean and covariance matrix C , the likelihood function is

$$L(\underline{\beta}/\underline{z}^*) = (2\pi|C|)^{-1/2} \exp[(1/2)(\underline{z}^* - \underline{z})^T C^{-1}(\underline{z}^* - \underline{z})] \quad (3.4a)$$

where $\underline{z}^*$ is a vector incorporating the available transport system response and formation property data given by $\underline{z}^* = (\underline{r}^*, \underline{p}^*)^T$, where $\underline{r}^*$ is the vector of measurements of the response of the transport domain, and $\underline{p}^*$ is the vector of the measured values of the model parameters vector $\underline{p}$; $\underline{\beta}$ is a vector of all unknown parameters, given by $\underline{\beta} = (\underline{p}, \underline{s})^T$, where $\underline{s}$ is a vector of the unknown statistical parameters $(\sigma_r^2, \sigma_{pj}^2)^T$.

The error covariance matrix C is block diagonal, its diagonal components being the covariance of the prior system response errors, $C_r = \sigma_r^2 V_r$, and the covariance of the prior errors associated with the model parameters p_j , $C_p = \sigma_{pj}^2 V_p$, where σ_r^2 and σ_{pj}^2 are either known or unknown positive scalars, and V_r and V_p are known symmetric positive definite matrices. Maximum likelihood (ML) estimates are generally obtained by minimizing the

log-likelihood criterion

$$\phi = -2\log[L(\underline{\beta}/\underline{z}^*)] \quad (3.4b)$$

In the special case in which σ_r^2 and σ_{pj}^2 are fixed, the log-likelihood criterion (3.4b) is equivalent to the generalized least squares criterion that may take into account prior information about the model parameters, i.e.,

$$\phi = \phi_r + \sum_j \lambda_j \phi_p \quad (3.5a)$$

where the response residual criterion ϕ_r is given by

$$\phi_r = [r^*(t; \Theta) - \hat{r}(t; \Theta; \hat{p})]^T V_r^{-1} [r^*(t; \Theta) - \hat{r}(t; \Theta; \hat{p})] \quad (3.5b)$$

where $\underline{r}^*$ and $\hat{\underline{r}}$ represent measured and computed (with parameters $\hat{\underline{p}}$) system response at time t , respectively. The parameter penalty criterion ϕ_p is given by

$$\phi_p = (\underline{p}^* - \hat{\underline{p}})^T V_p^{-1} (\underline{p}^* - \hat{\underline{p}}) \quad (3.5c)$$

where $\underline{p}^*$ represents prior estimates of the parameters $\underline{p}$, and $\lambda_j = \sigma_r^2 / \sigma_{pj}^2$, ($j=1$ to N_p) are relative weights assigned to the penalty criteria.

3.2.2 Posedness of the Inverse Problem

For our case, the inverse problem can be defined as follows: given a functional relationship between the response, $r(t)$ of the transport domain and the set of parameters describing the formation heterogeneity, $\underline{p}$ (i.e., $r=F(\underline{p})$), determine the parameters on the basis of $r(t)$ and the inverse relationship $\underline{p}=I(r)$. This problem is said to be properly posed [Carrera and

Neuman, 1986] if and only if (i) a solution exists; (ii) the solution is unique for any given r ; and (iii) the solution is stable. If the inverse problem fails to satisfy one or more of these requirements, it is then referred to as being ill-posed.

Ill-posedness of the inverse problem may be attributed to nonuniqueness, nonidentifiability, or instability. Detailed discussion on how each of them may affect the behavior of the inverse solution is given elsewhere [e.g., Carrera and Neuman, 1986]; here we will refer only to the essence of their discussion. Identifiability refers to the forward relationship, F ; if more than one parameter set p leads to a given response, r , the parameters are unidentifiable. In contrast, uniqueness refers to the inverse relationships, I ; when I represents the minimization of an estimation criterion, the inverse solution is nonunique whenever the criterion to be minimized is nonconvex, i.e., it has local minima or a global minimum at more than one point in the parameter space. In other words, if a given response $r(t)$ leads to more than one set of values of the parameter vector p , the inverse solution is nonunique. Stability means that small errors in the response data must not result in large changes in the estimated parameters. Instability may arise from a lack of or a poor degree of identifiability, and it is generally associated with an estimation criterion that is flat near the minimum.

It should be emphasized here that when the solution of the inverse problem is sought by minimizing a criterion based only on the response of the flow system (i.e., when the second term on the RHS of (3.5a) vanishes), identifiability is necessary, but not sufficient, for uniqueness. On the other hand, when the solution of the inverse problem is sought by minimizing a criterion based on the response as well as on prior information about the parameters ((3.5a)), identifiability is neither necessary nor sufficient for uniqueness.

3.2.3 Identifiability

To examine the question of identifiability, we addressed the forward relationships $r=F(p)$, considering each of the principal components of the displacement covariance tensor, $X_{ii}(t;\Theta)$ ($i=1$ to m) ((3.)) as a characteristic of the transport domain response, $r(t;\Theta)$. The response $r(t;\Theta)=X_{11}(t;\Theta)$ (or $r(t;\Theta)=X_{22}(t;\Theta)=X_{33}(t;\Theta)$) was calculated for a parameter space which covered a considerable range of values of the pertinent parameters. In this parameter space, contours of $r'(t;\Theta)=r(t;\Theta;p)/r(t;\Theta;p^*)$, where $p^*=(1,1,1,1)$ is a reference parameter vector, were calculated for various travel times. The contours of $r'(t;\Theta;p)=1$, calculated for several different travel times intersect only at one point ($p=p^*$) in the N_p -dimensional parameter space, indicating that the four parameters σ_w^2 , I_{wv} , e and A , are simultaneously identifiable. The contours of $r'(t;\Theta)=1$ as functions of σ_w^2 and I_{wv} , (e and A are fixed), and as functions of e and A (σ_w^2 and I_{wv} are fixed), for four different travel times (Fig. 3.1) clearly demonstrate this graphically.

The mathematical reasons for the shape of the contours of $r(t;\Theta)$ in Fig. 3.1 may be explained based on the structure of (3.2). It is seen that both σ_w^2 and I_{wv} and e and $g=(2J_1-1)AI_{wv}$ interact in a multiplicative manner in front of the integrals on the RHS of (3.2a) and in the three terms in the RHS of (3.2b), respectively. However, inasmuch as I_{wv} appears also in the three terms of in the RHS of (3.2b) and e appears also in the RHS of (3.2a) and in the three terms of (3.2b), σ_w^2 , I_{wv} , e and A are simultaneously identifiable. This can be proved with relative ease for the special case of $A=0$ and $e=1$, for which the components X_{ii} ($i=1$ to 3) have closed-form analytical expressions [e.g., Dagan, 1984], given by

$$X_{11}(t; \Theta) = 2I_{wv}^2 \sigma_w^2 \left[-\frac{8}{3} - \frac{8I_{wv}^3}{t^3 U^3} + \frac{4I_{wv}}{tU} + \frac{tU}{I_{wv}} + \frac{8I_{wv}^3(1 + \frac{tU}{I_{wv}})}{\exp(\frac{tU}{I_{wv}}) t^3 U^3} \right] \quad (3.6a)$$

$$X_{22}(t; \Theta) = X_{33}(t; \Theta) = 2I_{wv}^2 \sigma_w^2 \left[\frac{1}{3} + \frac{4I_{wv}^3}{t^3 U^3} - \frac{I_{wv}}{tU} - \frac{I_{wv}^3(2 + \frac{tU}{I_{wv}})^2}{\exp(\frac{tU}{I_{wv}}) t^3 U^3} \right] \quad (3.6b)$$

where both σ_w^2 and I_{wv} depend on Θ . The proof follows from the fact that if two different sets of (σ_w^2, I_{wv}) and (σ_w^2, I_{wv}) yield the same response, say, $r(t; \Theta) = X_{11}(t; \Theta)$, then substitution of each set in turn into (3.6a) and subtraction of one equation from the other gives

$$\begin{aligned} & 2\exp(-t'-t'') [24\exp(t'') I_{wv}^5 \sigma_w^2 - 24\exp(t'+t'') I_{wv}^5 \sigma_w^2 - 24\exp(t') I_{wv}^5 \sigma_w^2 \\ & + 24\exp(t'+t'') I_{wv}^5 \sigma_w^2 + 24\exp(t'') I_{wv}^4 \sigma_w^2 tU - 24\exp(t') I_{wv}^4 \sigma_w^2 tU \\ & + 12\exp(t'+t'') I_{wv}^3 \sigma_w^2 t^2 U^2 - 12\exp(t'+t'') I_{wv}^3 \sigma_w^2 t^2 U^2 \\ & - 8\exp(t'+t'') I_{wv}^2 \sigma_w^2 t^3 U^3 + 8\exp(t'+t'') I_{wv}^2 \sigma_w^2 t^3 U^3 + 3\exp(t'+t'') I_{wv} \sigma_w^2 t^4 U^4 \\ & - 3\exp(t'+t'') I_{wv} \sigma_w^2 t^4 U^4] / 3t^3 U^3 = 0 \end{aligned} \quad (3.7)$$

where $t' = tU/I_{wv}$, and $t'' = tU/I_{wv}$. It can be shown that for positive σ_w^2 and I_{wv} and for finite $t > 0$, (3.7) has only one solution, $\sigma_w^2 = \sigma_w^2$ and $I_{wv} = I_{wv}$. The same result can be obtained for $X_{ii}(t; \Theta)$, $i=2,3$ ((3.6b)).

3.2.4 Uniqueness

When the inverse relationships, $\mathbf{I}$ represent the minimization of an estimation criterion, a sufficient condition for uniqueness is that the estimation criterion be convex within the

domain of definition of the parameters. This requirement is satisfied if the Hessian matrix is positive definite [Carrera and Neuman, 1986]. We will address here the situation in which the parameter vector $\mathbf{p}$ is estimated by minimizing the least-squares criterion (3.5). It is assumed here that error-free measurements of the response at different travel times are available. For illustration purposes, the response was obtained from (3.2) with $\mathbf{p}=\mathbf{p}^*$, considering the three components of (3.2) jointly, i.e., $r^*(t_\ell, \Theta) = \Sigma X_{ii}(t_\ell; \Theta; \mathbf{p}^*)$, $t_\ell = \ell \delta t$, ($\ell = 1$ to 25 and $\delta t = 0.8$). For the case in which prior information on the parameters is absent, $\phi = \phi_r$ (3.5) was calculated for a parameter space which covered a considerable range of values of the pertinent parameters. A minimum (i.e., $\phi \rightarrow 0$) was reached at only one point ($\mathbf{p}=\mathbf{p}^*$) in the parameter space, suggesting that in this case the solution of the inverse solution was unique. This can be demonstrated graphically (Fig. 3.2) for the special case of $A=0$ and $e=1$, for which the components X_{ii} ($i=1$ to 3) are given by the closed-form analytical expressions (3.6). In this case ϕ_r ((3.5b)) is a minimum, when $\partial \phi_r / \partial \sigma_w^2 = 0$ and $\partial \phi_r / \partial I_{wv} = 0$. Note that for a given travel time, the contours of $\partial \phi_r / \partial \sigma_w^2 = 0$ and $\partial \phi_r / \partial I_{wv} = 0$ coincide. For different travel times, however, they intersect only at one point ($\mathbf{p}=\mathbf{p}^*$) in the two-dimensional parameter space (Fig. 3.2) indicating that the inverse solution was unique.

For the ideal case of the error-free response data given by (3.2), this result is not surprising, since the parameters were shown to be simultaneously identifiable. In general, however, it is difficult to prove uniqueness mathematically. This stems from the fact that one cannot guarantee the positive definiteness of the Hessian matrix. For the estimation criterion (3.5), the Hessian is

$$\frac{\partial^2 \phi}{\partial p_i \partial p_j} = \frac{\partial^2 \phi_r}{\partial p_i \partial p_j} + \frac{\partial^2 \phi_p}{\partial p_i \partial p_j} \quad (3.8a)$$

Expanding (3.8a) yields

$$\frac{\partial^2 \phi}{\partial p_i \partial p_j} = 2 \left(\frac{\partial r}{\partial p_i} \right)^T V_r^{-1} \frac{\partial r}{\partial p_j} - 2(r^* - r)^T V_r^{-1} \frac{\partial^2 r}{\partial p_i \partial p_j} + 2V_p^{-1} \quad (3.8b)$$

The first term on the RHS of (3.8b) is positive semidefinite because the covariance matrix V_r is positive definite. The second term could be negative, while the third term is positive definite because of the positive definite covariance matrix, V_p . Note that, in the absence of prior information about p , the third term on the RHS of (3.8b) does not appear, hence, in this case, one cannot guarantee the positive definiteness of (3.8). The inclusion of prior information increases the chances that (3.8) will be positive definite, but it still cannot be guaranteed.

3.2.5 Stability

To investigate the stability of the inverse solution, we considered the case in which the input data are subject to random (measurement) error, assuming that the data error can be represented as a $N(0, \sigma_r^2)$ term which is added to the "exact" error-free data. The error in the response data is quantified in terms of the relative quantity $CV_r = (\sigma_r^2)^{1/2} / r^*(t; \Theta)$, where $r^*(t; \Theta)$ is the "exact" error-free response, obtained as before from (3.2) with $p = p^*$.

We considered first the case in which no prior information on the model parameters is available. The results (for $CV_r = 0.2$) in terms of contours of $\phi = \phi_r$ as functions of σ_w^2 and I_{ww} , (e and A are fixed) and as functions of e and A (σ_w^2 and I_{ww} are fixed) are displayed in Figs. 3a and 4a, respectively. It is clearly demonstrated in these figures that when an error is introduced into the response data, the inverse solution is no longer unique. In other words, in this case, identifiability is not sufficient for uniqueness. As the data error increases, the

region associated with the smallest ϕ will extend over an increasing portion of the parameter space, i.e., the degree of nonuniqueness of the inverse solution increases with the error in the response data.

Next, we examine the effect on the behavior of the inverse solution, of incorporating prior information about the model parameters into the minimization algorithm, when the input data are subject to measurement error. We assume that the prior estimates of each of the parameters, p_j^* ($j=1$ to 4) is associated with an error characterized by $CV_{pj}=(\sigma_{pj}^2)^{1/2}/p_j^*=0.1$. The results (for $CV_r=0.2$) in terms of the contours of ϕ ((3.5)) as functions of σ_w^2 and I_{ww} , (e and A are fixed) and as functions of e and A (σ_w^2 and I_{ww} are fixed) are displayed in Figs. 3.3b-d and 3.4b-d, respectively. For $CV_r=0.2$, which may be considered as representing fairly moderate measurement error, when prior information is available for only one parameter (σ_w^2 or I_{ww} in Fig. 3.3b,c; e or A in Fig. 4b,c), the inverse solution behaves properly, as is evident from the minimum in these figures. Prior information on two of the model parameters (Fig. 3.3d or Fig. 3.4d) and smaller error in the prior estimates of the parameters (not shown here) will further enhance the likelihood of uniqueness and stability of the inverse solution. It should be noted, however, that when the data error is relatively large, the minimum may not exist, and the extent of the region associated with the smallest ϕ will increase with CV_r .

One of the reasons for the difficulty of proving stability stems from the fact that the error in the input response data may increase the chances that (3.8) will not be positive definite, and hence increase the likelihood of nonuniqueness of the inverse solution. In addition, poor prior estimates of the model parameters also may increase the likelihood of nonuniqueness, but appropriate weighing of the response data and the prior estimates should reduce the effect of poor prior estimates [Carrera and Neuman, 1986].

3.3 Prior Estimates of the Model Parameters

The above discussion suggests that the inclusion of prior information on the model parameters may increase the likelihood that (3.8) will be positive definite, although this cannot be guaranteed. Thus, the inclusion of prior estimates of the model parameters in the minimization algorithm may increase the likelihood that the resulting inverse problem will be well posed. Prior estimates of the model parameters may be obtained from direct measurements of $\log K$. Here, however, we will consider the situation in which direct measurements of $\log K$ are not available, and will focus on the determination of prior estimates of the model parameters from the response $r(t; \Theta)$. As will be shown below, prior estimates of the parameters of $C_{yy}(\xi; \Theta)$ for anisotropic formations can be determined from the behavior of the principal components of the displacement covariance tensor at the small t limit, $t \rightarrow 0$ and the large t limit, $t \rightarrow \infty$.

First, we employ the relationships between the statistics of the log-unsaturated conductivity and the velocity fields. Considering the motion of a streamline which, on the average, is parallel to the x_1 axis, the behavior of the principal components of $u_{ij}(\xi; \Theta)$ ((2.4)) is explained by continuity considerations [Rubin and Dagan, 1992]. Accordingly, the longitudinal component along the x_1 axis (the direction of the mean flow), $u_{11}(\xi_1, 0, 0)$, is positive and integration of (2.4) (for $i=j=1$) with respect to ξ_1 , along a direction parallel to the mean flow gives

$$u_{11}(0; \Theta) I_{u1}(\Theta) = U^2 \sigma_w^2(\Theta) I_{wv}(\Theta) \quad (3.9)$$

where $I_{u1}(\Theta)$ and $u_{11}(0; \Theta)$ are the correlation scale in the direction parallel to the mean flow and the variance, respectively, of the longitudinal component of velocity.

The equality (3.9) is independent of m and e as long as I_{wv} is defined by integration of

$C_{ww}(\xi; \Theta) = C_{ff}(\xi) + H^2(\Theta)C_{aa}(\xi) - 2H(\Theta)C_{fa}(\xi)$ with respect to ξ , along a direction parallel to the mean flow. Using the above considerations, the transverse velocity covariances along the x_1 axis, $u_{ii}(\xi_1, 0, 0; \Theta)$ ($i=2$ to m) must exhibit negative values as well; consequently, the integral of (5) (for $i=2$ to m , $i=j$) along a direction parallel to the mean flow is zero, irrespective of e and m .

On the other hand, the velocity variances, $u_{ii}(0; \Theta)$ ($i=1$ to m) depend on both e and m [Rubin and Dagan, 1992; Russo 1995a, 1997a] and can be expressed by

$$u_{ii}(0; \Theta) = \beta_{mi}(e, g) U^2 \sigma_w^2(\Theta) \quad (3.10)$$

where β_{mi} ($i=1$ to m) are coefficients which depend both on m and on the direction of the mean flow relative to the formation bedding.

Adopting (1.2) for the relationships between $\log K$ and ψ at the core scale, for mean flow in the vertical direction, $\beta_{mi}(e, g)$ ($i=1$ to m) for $m=2$ or $m=3$ are given [Russo, 1997b] by

$$\beta_{mi}(e, g) = \frac{1}{4\pi} \int_{-1}^{+1} \int_0^{2\pi} \frac{C_{mi} b_1 d\mu dr}{[(d_m^2 + r^2 e^{-2})^2 - r^2 e^{-4} g^2]^2} \quad (3.11a)$$

where b_1 is given by

$$b_1 = (d_m^2 + r^2 e^{-2})^2 - 3r^2 e^{-4} g^2 + [2|r^3| e^{-6} g^3 / (d_m^2 + r^2 e^{-2})] \quad (3.11b)$$

Note that for $m=3$, $\beta_{33}(e, g) = \beta_{22}(e, g)$ and calculation of $\beta_{mi}(e, g)$ ($i=1$ to 3) requires integration of the RHS of (3.11a) with respect to r only. At the small limit of g , $g \rightarrow 0$, analytical expressions of $\beta_{mi}(e)$ ($i=1$ to m) for $m=2$ and $m=3$, are given in Russo [1995a] and in Chapter 1.

Next, we employ the relationships between the behavior of the principal components of the displacement covariance tensor at $t \rightarrow 0$ and $t \rightarrow \infty$ and the statistics of the velocity fields. At

the small t limit, $t \rightarrow 0$, in agreement with Taylor's theory, and irrespective of m , X_{ii} ($i=1$ to m) grow quadratically with time, i.e.,

$$X_{ii}(t; \Theta) \rightarrow u_{ii}(0; \Theta)t^2, \quad t \ll I_{wv}(\Theta)/U \quad (3.12)$$

Differentiation of (3.12) twice with respect to t , and substitution of (3.11) in the resultant yields, after rearrangement

$$\sigma_w^2(\Theta) = \frac{1}{2\beta_{mi}(e, g)U^2} \left[\frac{d^2 X_{ii}(t; \Theta)}{dt^2} \right]_{t \rightarrow 0}, \quad i = 1 \text{ to } m \quad (3.13)$$

At the large t limit, $t \rightarrow \infty$, again in agreement with Taylor's theory, and irrespective of m , the longitudinal component of the displacement covariance tensor, X_{11} grows linearly with time, independently of e , i.e.,

$$X_{11}(t; \Theta) \rightarrow 2tu_{11}(0; \Theta)I_{u1}(\Theta)/U, \quad t \gg I_{wv}(\Theta)/U \quad (3.14)$$

Differentiation of (3.14) with respect to t and substitution of (3.9) in the resultant yields, after rearrangement

$$\sigma_w^2(\Theta)I_{wv}(\Theta) = \frac{1}{2U} \left[\frac{dX_{11}(t; \Theta)}{dt} \right]_{t \rightarrow \infty} \quad (3.15)$$

On the other hand, the large time behavior of transverse components of the displacement covariance tensor, X_{ii} ($i=2$ to m) depends on both m and e . For $m=3$, X_{ii} ($i=2$ to m) tend to constant values for finite e at the large t limit, $t \rightarrow \infty$, increasing with decreasing e . For $m=2$, the growth of X'_{22} becomes logarithmic with t , i.e., $dX_{22}/d(\log_e t) = t dX_{22}/dt$ tends to constant value for finite e as $t \rightarrow \infty$, increasing with decreasing e [Russo, 1997a].

Asymptotic constants X_{ii} ($i=2,3$) (for $m=3$) and $t dX_{22}/dt$ (for $m=2$) are calculated from

(3.2) at the limit $t \rightarrow \infty$ and can be expressed as

$$X_{ii}(t \rightarrow \infty; \Theta) = \gamma_3(e, g) \sigma_w^2(\Theta) I_{wv}^2(\Theta), \quad i=2,3, \quad m=3 \quad (3.16a)$$

$$tdX_{22}/dt(t \rightarrow \infty; \Theta) = \gamma_2(e, g) \sigma_w^2(\Theta) I_{wv}^2(\Theta), \quad m=2 \quad (3.16b)$$

where $\gamma_m(e, g)$, $m=2,3$ are coefficients which depend on m , given by

$$\gamma_m(e; g) = \frac{1}{2\pi} \int_{-1}^{+1} \int_0^{2\pi} \frac{C_{mi} b_m^\infty d\mu dr}{[(d_m^2 + r^2 e^{-2})^2 - r^2 e^{-4} g^2]^2} \quad (3.17a)$$

where $i=2$ for $m=2$, and $i=2$ or $i=3$ for $m=3$; for $m=2$, b_m^∞ is given by

$$b_2 = \frac{t' [(d_m^2 + r^2 e^{-2})^2 |r| t' + e^{-4} g^2 (2 - |r| t')]}{|r| \exp(|r| t')} - \frac{2t' e^{-4} g^2}{|r| \exp\left[\frac{r^2 e^{-2} g t'}{d_m^2 + r^2 e^{-2}}\right]} \quad (3.17b)$$

evaluated at the large t limit, $t \rightarrow \infty$, while for $m=3$, b_m^∞ is given by the right hand side of (3.2b) evaluated at the large t limit, $t \rightarrow \infty$. Analytical expressions of $\gamma_m(e)$ for the small limit of g , $g \rightarrow 0$, for both $m=2$ and $m=3$, are given in Russo [1995a] and in Chapter 1.

The system (3.13) (for $i=1,2$ or $i=1,3$ (for $m=3$)), (3.15) and (3.16) provides a set of four equations which can be solved for the four unknowns, σ_w^2 , I_{wv} , $e = I_{wv}/I_{yh}$ and $g = (2J_1 - 1)AI_{wv}$ as follows. Equating (3.13) for $i=1$ and $i=2$ gives

$$\frac{\beta_{m2}(e, g)}{\beta_{m1}(e, g)} = \frac{\left[\frac{d^2 X_{22}(t; \Theta)}{dt^2} \right]_{t \rightarrow 0}}{\left[\frac{d^2 X_{11}(t; \Theta)}{dt^2} \right]_{t \rightarrow 0}}, \quad m = 2, 3 \quad (3.18)$$

Substituting (3.13) (for $i=1$) in (3.15) and solving for I_{wv} gives

$$I_{wv}(\Theta) = \frac{\beta_{m1}(e, g) U \left[\frac{dX_{11}(t; \Theta)}{dt} \right]_{t \rightarrow \infty}}{\left[\frac{d^2 X_{11}(t; \Theta)}{dt^2} \right]_{t \rightarrow 0}}, \quad m = 2, 3 \quad (3.19)$$

Similarly, substituting (3.13) (for $i=2$) in (3.16) and solving for I_{wv} gives

$$I_{wv}(\Theta) = \left[\frac{2\beta_{m2}(e, g) U^2 Y_{m2}(t \rightarrow \infty; \Theta)}{\gamma_m(e, g) \left[\frac{d^2 X_{22}(t; \Theta)}{dt^2} \right]_{t \rightarrow 0}} \right]^{1/2}, \quad m = 2, 3 \quad (3.20)$$

where $Y_{m2}(t \rightarrow \infty; \Theta) = (3-m)tdX_{22}/dt(t \rightarrow \infty; \Theta) + (m-2)X_{22}(t \rightarrow \infty; \Theta)$, and $m=2, 3$.

Finally, combining (3.19) and (3.20) yields, after rearrangement:

$$\beta_{m1}(e, g) \gamma_m(e, g) = \frac{2 Y_{m2}(t \rightarrow \infty; \Theta) \left[\frac{d^2 X_{11}(t; \Theta)}{dt^2} \right]_{t \rightarrow 0}}{\left[\left[\frac{dX_{11}(t; \Theta)}{dt} \right]_{t \rightarrow \infty} \right]^2}, \quad m = 2, 3 \quad (3.21)$$

For a given m , the values of e and g are determined by finding the point in the (e, g) plane for which an isoline of the product $\beta_{m1}(e, g)\gamma_m(e, g)$ (calculated from (3.21)) intersects an isoline of the ratio $\beta_{m2}(e, g)/\beta_{m1}(e, g)$ (calculated from (3.18)). Once e and g have been determined and the values of $\beta_{mi}(e, g)$, $i=1, 2$ and $\gamma_m(e, g)$ have been evaluated from (3.11) and (3.17), respectively, $\sigma_w^2(\Theta)$ is determined from (3.13) (for either $i=1$ or $i=2$), while $I_{wv}(\Theta)$ is determined from either (3.19) or (3.20). Contour lines of the ratio $\beta_{m2}(e, g)/\beta_{m1}(e, g)$ (the iso-lines that descend from the left hand side of the ge -plane to its right hand side) superimposed on contour lines of the product $\beta_{m1}(e, g)\gamma_m(e, g)$ (Figs. 3.5 and 3.6) illustrate the solution of (3.18) and (3.21) for e and g , graphically for two- and three-

dimensional flow domains, respectively.

It should be emphasized that in practical situations of vadose-zone transport, the observed travel distance may be small as compared with the travel distance required for the plume to reach its asymptotic, Fickian behavior. Thus, in such circumstances, data for the response at the large t limit may not be available, and the determination of prior estimates of the model parameters should be based on data for the response at the small t limit only. Considering the fact that the ratio $\beta_{m2}(e,g)/\beta_{m1}(e,g)$ is relatively insensitive to g for a considerable range of values of g (Figs. 5 and 6), prior estimates of $e=I_{wv}/I_{wh}$ can be determined from the response at the small t limit using (3.18) evaluated at the small g limit.

3.4 Illustrative Example

To demonstrate the procedure for estimating the parameters of $\log K$ covariance through inverse problem methodology, we employed the results of simulated transport by quasi-steady-state flows [Russo et al., 1994a] of a pulse of a tracer solute in a vertical cross-section of a hypothetical but realistic, heterogeneous, partially saturated soil. The simulations (each associated with a different predetermined capillary pressure head, ψ_0 imposed on the entry zone) were performed by combining a statistical generation method for producing adequately resolved realizations of the heterogeneous formation properties, with efficient numerical methods for solving the partial differential equations governing flow and transport in unsaturated, heterogeneous soils. For more details see Russo et al. [1994a].

Results of these simulations have been demonstrated in terms of the distribution of the simulated resident concentrations of solute, $c_r(x_1, x_2; t)$ in the vertical cross section of the heterogeneous soil (Fig. 3 in Russo et al., 1994a) for various mean water saturations, $\Theta(\psi_0)$, and scaled travel distances, $t' = Ut/I_{f1}$. Second spatial moments $S_{ii}(t; \Theta)$ ($i=1,2$) were

calculated from the spatial distribution of the simulated $c_r(x_1, x_2; t)$ using (3.1) (with x_3 being suppressed) and, in turn, were used to calculate principal components of the particle displacement covariance tensor, $X_{ii}(t; \Theta) = S_{ii}(t; \Theta) - S_{ii}(0; \Theta)$ ($i=1, 2$).

It should be emphasized that the example illustrated here is an ideal case, in the sense that the simulated transport provides much more detailed information (that is unaffected by uncertainty due to measurement errors or inadequate sampling) on the solute spreading than is attainable in practice from field investigations. To consider a more realistic case, in which the response data are subject to random (measurement) error, a $N(0, \sigma_r^2)$ term was added to the "exact", error-free simulated $X_{ii}(t; \Theta)$ data. The relative error in the response data was $CV_r = (\sigma_r^2)^{1/2} / X_{ii}(t; \Theta) = 0.25$. The resultant $X_{ii}(t; \Theta)$ ($i=1$ to 2) data are depicted in Fig. 3.7.

It is evident (Fig. 3.7) that the simulated plumes did not reach their asymptotic, Fickian behavior, particularly in cases associated with lower Θ . Thus, prior estimates of the covariance parameters can be obtained from the small time behavior of the plume only. Estimates of d^2X_{ii}/dt^2 ($i=1, 2$) at the small t limit, $t \rightarrow 0$ (Table 3.1) were used to determine prior estimates of the anisotropy ratio, e using (3.18) evaluated at $g \rightarrow 0$. In the case of two-dimensional flow ($m=2$), the solution of (3.18) evaluated at $g \rightarrow 0$ yields

$$e = \frac{1}{2} \left[\frac{(d^2X_{11}(t; \Theta)/dt^2)_{t \rightarrow 0}}{(d^2X_{22}(t; \Theta)/dt^2)_{t \rightarrow 0}} - 1 \right] \quad (3.22)$$

The resultant prior estimates of e (Table 3.1) are in relatively good agreement with the value of $e=0.25$ used as input in generating realizations of the parameters of $\log K(\Theta)$ for the transport simulations [Russo et al., 1994a].

Both the longitudinal and the transverse components of the particle displacement covariance tensor were taken into account as representatives of the response of the transport domain, i.e., $r^*(t; \Theta) = X_{11}(t; \Theta) + X_{22}(t; \Theta)$. It was assumed that the error in the prior

estimates of $e=p_3$ is characterized by $CV_{p_3}=\sqrt{\sigma_{p_3}^2/p_3^*}=0.1$. Owing to the fact that the objective function (3.5) is nonlinear in the model parameters, the minimization procedure was carried out iteratively. Gauss quadrature was used to evaluate the integrals in (3.2) (for $i=1,2$) in order to obtain estimates of the response $r(t;\Theta;p)=X_{11}(t;\Theta;p)+X_{22}(t;\Theta;p)$ in (3.5). Estimates of the model parameters were obtained by minimizing (3.5) by the Levenberg-Marquardt method [Press et al., 1992] to ensure that the optimization proceeded in a descent direction. The results for various mean water saturations, Θ are summarized in Table 3.2. The resultant fitted responses, $r(t;\Theta;p)$ are depicted in Fig. 3.7.

Inclusion of prior estimates of e in the estimation criterion yields parameter estimates which differ from those obtained in the absence of prior information (Table 3.1). The fitted responses, $r(t;\Theta;p)$ associated with the two cases, however, are almost indistinguishable (Fig. 3.7). For both sets, the agreement between the simulated and the fitted responses, was very good, as is indicated by the coefficient of determinations, $R^2 \approx 0.99$. Because of the "noise" in the simulated data, however, there will be a relatively large number of combinations of σ_w^2 , I_{ww} , e and A (the values of which will depend on the initial guesses of these parameters), for which the results of the inversion (in terms of the residual sum of squares, RSS) will be very similar. This phenomenon was found also in the analysis of the Cape Cod transport data (Deng et al., 1993), in which the optimal adaptive estimates of $\sigma_f^2=0.26$ and $I_f=3.2m$ yielded the same fit to the observed spatial moment data as did the initial estimates of $\sigma_f^2=0.24$ and $I_f=3.5m$ obtained from the experimental semivariogram of $\log K_s$.

This stems from the fact that in the absence of prior information on the model parameters in the estimation criterion, relatively small noise in the data may induce instability in the inverse solution (see Figs. 3.3 and 3.4 and the related discussion). On the other hand, when prior information on e (Table 3.1) is included in the estimation criterion, the number of

degrees of freedom decreases, the estimated value of e approaches its prior estimate (Table 3.2), and the estimated values of the other parameters adjust themselves accordingly. Although the inclusion of prior information on the parameters in the estimation criterion may enhance the likelihood of uniqueness and stability of the inverse solution (see Figs. 3.3 and 3.4 and the related discussion), because prior information is available on one parameter only, the resultant inverse solution is still nonunique.

Nevertheless, the inclusion of prior information on e in the estimation criterion, considerably reduced the uncertainty about the parameter estimates, as compared with the case in which no prior information on the parameters was considered, as is indicated by the respective standard errors of estimation, SE (Table 3.2). It should be emphasized, however, that the SE values in Table 3.2 are based on the Cramer-Rao theorem, which gives an estimate of the lower bound of the covariance matrix of estimation errors, that, in turn, is approximated by the Fisher Information matrix. Since this estimate of SE and the Student's t statistic used for evaluating the confidence limits for the parameters are taken from linear regression analysis, it will hold only approximately for the nonlinear problem. This approach will give a good approximation to the SE values, to the extent that the sum of squares is locally linear in the parameters. Thus, these results should be used with caution.

The logK variance, $\sigma_y^2(\Theta)$ and correlation scale, $I_{yv}(\Theta)$ estimated from the simulated transport experiments by means of the proposed procedure (*i.e.*, from $\sigma_w^2(\Theta)$, $I_{wv}(\Theta)$, e and A using (9)) are in reasonably good agreement with those estimated directly from the simulated log-unsaturated conductivity fields (Table 3.3). It should be emphasized here that in the transport simulations of Russo et al. [1994a], the van Genuchten [1980] parametric expressions were adopted for the local $K(\psi)$ and $\Theta(\psi)$ relationships. On the other hand, in the approach adopted in the present Chapter, Gardner's [1958] simplified expression ((1.2))

was adopted for the local $K(\psi)$ relationships, while the simplified expression of Russo [1988] was adopted for the local $\Theta(\psi)$ relationships. A procedure to convert the parameters of the van Genuchten expressions (Table 1 in Russo et al., 1994b) to the "equivalent" parameter α of the Gardner-Russo expressions, described elsewhere (Appendix in Russo et al., 1994b), yields $A = \langle \alpha \rangle = 2.5\text{m}^{-1}$, in reasonably good agreement with the values of A in Table 3.2.

3.5 Concluding Remarks

The feasibility of estimating parameters of the logK covariance by inversion of an approximate solution of the transport problem under unsaturated flow conditions, employing spatial moments of the plume of a solute tracer at various travel times as input data, was analyzed in this Chapter. An example involving simulated transport of a pulse of a tracer solute by quasi-steady-state, unidirectional vertical, unsaturated flow was used to illustrate the inversion procedure. The main findings of this study are summarized as follows:

- (i) Using an approximate solution of the transport problem, based on a general Lagrangian description of the transport and a stochastic continuum description of the unsaturated flow, the model parameters are simultaneously identifiable; consequently, a unique solution may be obtained when error-free response data are available.
- (ii) A relatively small "noise" in the response data is sufficient to aggravate the likelihood of the ill-posedness of the inverse problem owing to instability of the solution. In this case, the inclusion of prior information on the model parameters in the estimation criterion reduces the degree of ill-posedness of the inverse problem, and might lead to a stable and unique solution even when the response data are associated with a considerable measurement error.
- (iii) The inclusion of prior information about the model parameters in the estimation criterion is not sufficient to guarantee uniqueness and stability in all cases. This is so because the

sufficient condition for uniqueness (i.e., the convexity of the estimation criterion in the parameter space, which, in turn, is satisfied when the Hessian matrix is positive definite) cannot be guaranteed in all cases.

(vi) Using the aforementioned approximate solution of the transport problem, prior estimates of the model parameters can be determined from the small and the large time behavior of the plume. When data on the response at the large time limit are not available, prior estimates of the anisotropy ratio, $e = I_{wv}/I_{wh}$ can be determined from the response at the small time limit only.

(v) The fitted responses based on results of inversions with or without prior estimates of e are almost indistinguishable. Estimates of the parameters in the latter case, however, are associated with a considerable uncertainty. The inclusion of prior information on a single parameter, e , in the estimation criterion, may significantly reduce the uncertainty about the parameters, as compared with the case in which no prior information on the parameters is considered.

Before concluding this Chapter we would like to emphasize the limitations of this study which might restrict direct field-scale application of the proposed approach. The theoretical framework of the proposed approach is based on small perturbations, first-order approximations of the velocity covariance tensors and the Lagrangian displacement tensors. Consequently, the approach cannot be applied to formations of large heterogeneity. The simplifying assumptions regarding the local log-unsaturated conductivity function ((1.2)) and the constant and uniform in space Θ (for a given mean capillary pressure head), might also limit the applicability of the proposed method. A discussion of these limitations is given in Chapter 1 and in Russo [1995b]. Furthermore, the theoretical framework of the proposed approach is based on ensemble mean statistics, while analyses of the transport data are based

on a single realization (a transport experiment or, as in the aforementioned example, a transport simulation). If the solute inlet zone is sufficiently large to ensure ergodicity, the discrepancy between single-realization statistics and ensemble mean statistics might be reduced significantly. In principle, non-ergodic transport can be analyzed with the same theoretical framework, introducing the covariance tensor of the trajectories of two particles originating from two points $\underline{a}'$ and $\underline{a}''$ in the solute injection area, $X_{ij}(t, \underline{a}', \underline{a}''; \Theta)$ ($i, j = 1, 2, 3$), [Dagan, 1991], rather than the one-particle displacement covariance ((1.16b)). The case of non-ergodic transport, however, was not addressed here and is left for future investigation.

Finally, we would like to emphasize that determination of the time behavior of the spatial moments of a real solute plume by field experiment, especially at relatively large times might be cumbersome and expensive. Furthermore, in practice, estimates of d^2X_{ii}/dt^2 ($i = 1, 2$) at the small t limit, $t \rightarrow 0$ and estimates of dX_{11}/dt and X_{22} (or $t dX_{22}/dt$) at the large t limit, $t \rightarrow \infty$, which are required in order to determine prior estimates of the model parameters by means of (3.18) and (3.21) might be subject to uncertainty due to inadequate sampling of the solute concentrations in time and/or space. The issue of measurement errors and/or partial sampling was not addressed here, however, and is left for future investigation.

With these limitations in mind, and considering those circumstances in which direct measurements of $\log K$ are not available, but measurements of the response of the transport domain are available, we believe that the approach presented in the present Chapter provides a theoretical framework for a procedure for characterizing the $\log K$ covariance on the field scale, at least to a first-order approximation. Controlled field-scale experiments and simulations of solute transport through heterogeneous, unsaturated soils are required in order to test the findings of this study further, before practical tools for the estimation of the $\log K$ covariance parameters can be provided.

4. Numerical Analysis of Flow and Transport in a Three-Dimensional Partially Saturated Heterogeneous Soil

4.1 Theoretical Considerations

Simulation of Transport in Heterogeneous, Partially Saturated Soil

Our purpose here is to simulate, on the field scale the transport of both passive and reactive solutes borne by water in partially saturated heterogeneous soil. We consider a three-dimensional flow domain that spans several meters in both horizontal and vertical directions, and will analyze the transport problem by means of physically based flow and transport models and a stochastic presentation of the soil properties that affect water flow and solute transport. The approach undertaken here is a "single realization" approach [e.g., Ababou, 1988; Russo, 1991; Polmann et al., 1991; Russo et al., 1994; Tseng and Jury, 1994], that may be understood as quantifying the macroscopic spreading of a single plume for particular site-specific applications. It should be distinguished from the ensemble macrodispersive flux that accounts for differences among the trajectories of random concentration replicates over the ensemble. Note that if the solute inlet zone is sufficiently large to ensure ergodicity, the discrepancy between single-realization statistics and ensemble mean statistics might be reduced significantly [Dagan, 1989].

Governing Partial Differential Equations

We assume here that the water flow is described locally by the Richards equation, the physical parameters of which are visualized as realizations of stationary random space functions (RSFs). It is further assumed that the transport of both the passive and the reactive

solute is described locally by a convection-dispersion equation (CDE). The reactive solute may exchange with the solid phase of the soil but does not undergo degradation (chemical and/or biological) and/or volatilization (conservative solute).

In a Cartesian coordinate system (x_1, x_2, x_3) , where x_1 is directed vertically downwards, assuming local isotropy, the "mixed" form of the Richards equation, governing saturated-unsaturated flow in the presence of water uptake by the plant roots is:

$$\frac{\partial \theta}{\partial t} = \sum_{i=1}^3 \sum_{j=1}^3 \frac{\partial}{\partial x_i} \left[K \frac{\partial \psi}{\partial x_j} \right] - \frac{\partial K}{\partial x_1} - S_w \quad (4.1)$$

where t is time; $\psi = \psi(\underline{x}, t)$ is capillary pressure head; $\theta = \theta(\underline{x}, t)$ is volumetric water content; $K = K(\psi, \underline{x})$ is conductivity; and $S_w = S_w(\underline{x}, t)$ is a sink term representing water uptake by plant roots.

Assuming a linear and reversible adsorption isotherm for the partitioning of the solute between the solid and liquid phases, the equation governing the transport of a reactive, conservative solute is:

$$\frac{\partial [(\theta + \rho_b K_d) c]}{\partial t} = \sum_{i=1}^3 \sum_{j=1}^3 \frac{\partial}{\partial x_i} \left\{ \theta D_{ij} \frac{\partial c}{\partial x_j} \right\} - \sum_{i=1}^3 \frac{\partial (u_i \theta c)}{\partial x_i} \quad (4.2)$$

where c is the resident solute concentration, expressed as mass per unit volume of soil solution; K_d is the partitioning coefficient; ρ_b is bulk density; u_i ($i=1,2,3$) are components of the pore water velocity vector; and D_{ij} ($i,j=1,2,3$) are components of the pore-scale dispersion tensor. Neglecting molecular diffusion, D_{ij} are given [Bear, 1972] as:

$$D_{ij} = \lambda_T |u| \delta_{ij} + (\lambda_L - \lambda_T) u_i u_j / |u| \quad (4.3)$$

where λ_L and λ_T are the longitudinal and the transverse pore-scale dispersivities; δ_{ij} is the

Kronecker delta (i.e., $\delta_{ij}=1$, if $i=j$, and $\delta_{ij}=0$ if $i \neq j$); and $|u| = (u_1^2 + u_2^2 + u_3^2)^{1/2}$.

The Sink Term in (4.1)

It is assumed here that locally, the rate of water uptake by roots is proportional to the unsaturated conductivity and to the difference between the total pressure head at the root-soil interface, Ψ_r and the corresponding capillary pressure head of the soil. According to this approach [i.e., Nimah and Hanks, 1973a; Feddes et al., 1974, Bresler, 1987], the sink term S_w in (4.1) is:

$$S_w(x,t) = - R_e(x,t) K[\psi(x,t)][\Psi_r(t) - \psi(x,t) - \Pi(x,t)] \quad (4.4)$$

where Π is the osmotic pressure head of the soil solution and R_e , the root effectiveness function, is proportional to the specific area of the soil-root interface and inversely proportional to the impedance of the soil-root interface, and can be estimated from root distribution data [e.g., Nimah and Hanks, 1973a,b].

Characterization of the Flow and Transport Parameters

The properties of the soil and/or the chemicals that are here hypothesized to control the field-scale solute spread are the soil hydraulic properties, characterized by the $K(\psi)$ and the $\theta(\psi)$ relationships and the partitioning coefficient, K_d . These soil properties vary in space in an irregular fashion, and the length scales of these variations are much greater than the pore scale. To quantify the spatial variations in these properties, we regard the soil as a continuum, the properties of which are continuous functions of the spatial coordinates. The elementary volume (REV) representing the soil properties of the field is characterized by a macroscopic scale that is small in comparison with the scale of the field heterogeneities, but

contains many pores. Our main concern is the effect of the spatial variations in the aforementioned soil properties on solute transport. Deterministic, constant values, therefore, were adopted for pore-scale dispersivities, $\lambda_L = 2 \times 10^{-3} \text{m}$ and $\lambda_T = 1 \times 10^{-4} \text{m}$, the bulk density, $\rho_b = 1200 \text{ kg/m}^3$. Furthermore, it was assumed that the root effectiveness function is time-invariant, deterministic function of the soil depth only, *i.e.*, $R_e(\underline{x}, t) = R_e(\underline{x}_1)$. Root distribution data from Mantell and Goell [1972] with rooting depth of 1.5m, were used to estimate $R_e(\underline{x}_1)$ (Fig. 4.1a).

To simplify the analysis, it is assumed that the local $K(\psi)$ and $\theta(\psi)$ relationships are described by the van Genuchten [1980] parametric expressions. Ignoring hysteresis and local anisotropy, considering the capillary pressure head, ψ as the dependent variable, they read:

$$\Theta(\psi, \underline{x}) = \left\{ \frac{1}{1 + [\beta(\underline{x})\psi]^{n(\underline{x})}} \right\}^{m(\underline{x})} \quad (4.5)$$

$$K(\psi, \underline{x}) = K_s(\underline{x}) \frac{\{1 - [\beta(\underline{x})\psi]^{n(\underline{x})-1} \{1 + [\beta(\underline{x})\psi]^{n(\underline{x})}\}^{-m(\underline{x})}\}}{\{1 + [\beta(\underline{x})\psi]^{n(\underline{x})}\}^{m(\underline{x})/2}} \quad (4.6)$$

where ψ is expressed here as a positive entity, $\Theta = (\theta - \theta_r) / (\theta_s - \theta_r)$, is the effective water saturation; θ_s and θ_r are the saturated and residual water contents, respectively; K_s is the saturated conductivity; β and m are parameters which are related to the soil pore size distribution, and $n = 1/(1-m)$.

It is assumed further that each parameter in (4.5) and (4.6) and the partition coefficient, K_d , denoted by $p(\underline{x})$, may be considered as a second-order stationary, statistically anisotropic RSF, characterized completely by a constant mean, $\langle p(\underline{x}) \rangle$, independent of the spatial position, and a covariance function, $C_{pp}(\underline{x}, \underline{x}')$ that, in turn, depends on the separation vector, $\underline{\xi} = \underline{x} - \underline{x}'$, and not on $\underline{x}$ and $\underline{x}'$ individually. A three-dimensional, exponential covariance (1.4)

is adopted here for $p(\underline{x})$.

In line with field studies [e.g., Byers and Stephans, 1983; Sudicky, 1986], axisymmetric anisotropy is adopted for $C_{pp}(\underline{x})$, i.e., $I_{pv}=I_{p1}$ and $I_{ph}=I_{p2}=I_{p3}$ are the characteristic length scales of $p(\underline{x})$ in the vertical (longitudinal) direction, and in the horizontal plane, respectively. Statistical parameters of the various soil parameters of (4.5) and (4.6) were adopted from the Bet Dagan trench [Russo and Bouton, 1992] and are summarized in Table 1. Inasmuch as detailed information on the spatial distribution of K_d in the Bet Dagan field are not available, the mean value and the variance of $\log K_d$ were adopted from a series of batch sorption tests using bromacil and Bet Dagan soil [Yaron, B., personal communication]. Similarly to Burr et al. [1994], the correlation scales of $\log K_s$ were adopted for $\log K_d$.

Generation of the Flow and Transport Parameters Field

With a "single realization" approach [e.g., Ababou, 1988; Russo, 1991], inference of statistical moments of the distribution of the pertinent soil properties and of the relevant flow-attributed variables requires a flow domain that spans a sufficient number of correlation scales of the relevant soil properties. In addition, in order to preserve details of the spatial structure of the soil properties, the size of the numerical cells must be small compared with the characteristic length scale of the heterogeneity of the relevant soil properties.

We considered a flow domain of 8m in each of the horizontal directions and 4m in the vertical direction. This provided a flow domain spanning eight and twenty correlation scales of $\log K_s$ in the respective directions. The flow domain was discretized into a large number of equalized cells, measuring 0.05m and 0.25m in the vertical and horizontal directions, respectively. Using the covariance function (1.4) and the values of σ_p^2 , I_{ph} and I_{pv} (Table 1) the turning bands method [Tompson et al., 1989] was used to generate independent

realizations of $\log K_s$, $\log \beta$, n , θ_s and θ_r on each of the $32 \times 32 \times 80$ nodes of the flow domain grid. Considering the physically plausible situation [e.g., Robin et al., 1991] in which $\log K_d$ is negatively correlated with $\log K_s$, the realization of $\log K_d$ was generated from that of $\log K_s$ using the relationship:

$$\log K_d(x) = \mu_g + (\log K_s(x) - \mu_f) \rho_{fg} \sqrt{(\sigma_g^2 / \sigma_f^2)} + \sqrt{(1 - \rho_{fg}^2)} \sigma_g R_N \quad (4.7)$$

where μ_f and μ_g and σ_f^2 and σ_g^2 are the mean values and the variances of $\log K_s$ and $\log K_d$, respectively, ρ_{fg} is the cross-correlation coefficient between $\log K_s$ and $\log K_d$, and R_N is a random number taken from the normal distribution $N(0,1)$.

Sample autocorrelation functions (ACFs), estimated from single realizations of the input parameters were found to be in relatively good agreement with the theoretical ACFs used to generate realizations of the parameters field. Values of $K(\theta)$ and $\psi(\theta)$ were generated for each node of the flow domain from the constitutive relations (4.5) and (4.6) by means of the generated realizations of the aforementioned parameters.

Boundary and Initial Conditions

For the analyses presented here, we considered the movement of both passive and reactive solute in a flow domain, Ω , consisting of an initially solute-free soil with a uniform initial capillary pressure head, $\psi_i = 3 \text{ mH}_2\text{O}$. Water is infiltrated into the soil by a time-dependent, spatially invariant potential flux, $q_0(t) > 0$, imposed on the entire soil surface. Water may leave the flow system through the upper boundary ($x_1 = 0$) by evaporation ($q_0 < 0$) and through the lower boundary ($x_1 = L_1$) by gravity flow. There is no water flow across the vertical planes located at $x_2 = 0$ and $x_2 = L_2$ and $x_3 = 0$ and $x_3 = L_3$, for which the normal derivatives of ψ vanish. For the flow, the appropriate boundary and initial conditions are:

$$-K(\psi)\frac{\partial\psi}{\partial x_1} + K(\psi) \leq |q_0(t)|, x_1=0, 0 \leq x_2 \leq L_2, 0 \leq x_3 \leq L_3, t > 0 \quad (4.8a)$$

$$\frac{\partial\psi}{\partial x_1} = 0, x_1=L_1, 0 \leq x_2 \leq L_2, 0 \leq x_3 \leq L_3, t > 0 \quad (4.8b)$$

$$-K(\psi)\frac{\partial\psi}{\partial x_2} = 0, x_2=0, x_2=L_2, 0 \leq x_1 \leq L_1, 0 \leq x_3 \leq L_3, t > 0 \quad (4.8c)$$

$$-K(\psi)\frac{\partial\psi}{\partial x_3} = 0, x_3=0, x_3=L_3, 0 \leq x_1 \leq L_1, 0 \leq x_2 \leq L_2, t > 0 \quad (4.8d)$$

$$\psi = \psi_i(x), \quad 0 \leq x_1 \leq L_1, 0 \leq x_2 \leq L_2, 0 \leq x_3 \leq L_3, \quad t=0 \quad (4.8e)$$

For transport, we considered a case in which a solute with concentration, c_0 , invades the soil during time, t_0 via a planar source of dimensions $(\rho_{22}-\rho_{21}) \times (\rho_{32}-\rho_{31})$ located at the soil surface. There is no solute transport across the soil surface outside the source, nor across the vertical planes located at $x_2=0$ and $x_2=L_2$ and $x_3=0$ and $x_3=L_3$, for which the normal derivatives of c vanish. Furthermore, a zero-gradient-boundary is specified at the bottom ($x_1=L_1$). For the transport, therefore, the appropriate boundary and initial conditions are:

$$\begin{aligned} c &= c_0, & 0 \leq t \leq t_0 \\ c &= 0, & t > t_0 \end{aligned} \quad x_1=0, \rho_{21} \leq x_2 \leq \rho_{22}, \rho_{31} \leq x_3 \leq \rho_{32} \quad (4.9a)$$

$$-\theta \sum_{j=1}^3 D_{1j} \frac{\partial c}{\partial x_j} + u_1 \theta c = 0, x_1=0, \rho_{21} \leq x_2 \leq \rho_{22}, \rho_{31} \leq x_3 \leq \rho_{32}, t > 0 \quad (4.9b)$$

$$-\theta \sum_{j=1}^3 D_{1j} \frac{\partial c}{\partial x_j} = 0, x_1=L_1, 0 \leq x_2 \leq L_2, 0 \leq x_3 \leq L_3, t > 0 \quad (4.9c)$$

$$\frac{\partial c}{\partial x_2} = 0, x_2=0, x_2=L_2, 0 \leq x_1 \leq L_1, 0 \leq x_3 \leq L_3, t > 0 \quad (4.9d)$$

$$\frac{\partial c}{\partial x_3} = 0, x_3=0, x_3=L_3, 0 \leq x_1 \leq L_1, 0 \leq x_2 \leq L_2, t > 0 \quad (4.9e)$$

$$c=0, 0 \leq x_1 \leq L_1, 0 \leq x_2 \leq L_2, 0 \leq x_3 \leq L_3, t=0 \quad (4.9f)$$

Implementation

We applied Eqs. (4.1) and (4.2), subject to (4.8) and (4.9), respectively, to investigate the transport of passive and reactive dissolved solutes (chloride and bromacil, respectively) by transient, unsaturated water flow under realistic soil, vegetative and climatic conditions. Details of the numerical approach used to approximate the governing equations (4.1) and (4.2), with boundary and initial conditions (4.8) and (4.9), respectively, are given in the Appendix D.

Crop and climatic conditions and agricultural practice typical of the central area of the coastal region of Israel, were adopted in the present study, in order to obtain realistic water uptake and surface boundary condition for the flow. A citrus orchard with a complete cover of the soil surface and a given root effectiveness function [Mantell and Goell, 1972] constant in time, was considered here (Fig. 4.1a). Irrigation dates, rates and amounts were adopted from the agricultural practice in this region with total amount of 700 mm/yr. Meteorological data from the weather station at Bet Dagan, were used to estimate potential evapotranspiration rates, $ET_p(t)$, as well as to provide rain rates and amounts during the winter (typical of Israel), with a total amount of 580 mm/yr. The estimated cumulative potential evapotranspiration was 1005 mm/yr. Water uptake by plants was implemented by a maximization iterative approach [Neuman et al., 1975]. In this approach, the rate of transpiration per unit area of the soil surface at time t , given by $T_r(t) = \int \Omega S_w(\underline{x}, t) d\underline{x}$, is maximized subject to two requirements: (i) actual rate of transpiration is not allowed to exceed the potential rate of transpiration, T_p and (ii) total pressure head at the root-soil interface, Ψ_r , is not allowed to fall below a critical value, Ψ_c , equivalent to the so-called wilting point of the soil-plant system (e.g., $\Psi_c = -150\text{m}$). Note that unlike in agricultural practice, in which solutes are continuously added to the flow system, a pulse application

((4.9a)) was considered in this study. Consequently, the osmotic pressure head of the soil solution, Π was not taken into account in the sink term (4.4). Note also that because of the complete coverage of the soil surface by the citrus orchard, it is assumed here that $ET_p = T_p$. Cumulative seasonal amounts of applied water (i.e., irrigation+rain, IR) and potential evapotranspiration used in this study as well as the simulated cumulative seasonal amount of actual evapotranspiration, $ET_a = \int T_r(t)dt$ are depicted in Fig. 4.1b.

For a given set of statistical parameters of the soil properties (Table 1) and given conditions at the soil surface, the movement of chloride and bromacil pulses was simulated using $L_1=4m$, $L_2=8m$, $L_3=8m$, $\rho_{21}=\rho_{31}=1.25m$, $\rho_{22}=\rho_{32}=6.75m$, and $c_0=1kg/m^3$. The total mass of solute entering the flow domain via the inlet zone at $x_1=0$ during a pulse of t_0 , is given as:

$$M_0 = \int_0^{t_0} \left[\int_{\rho_{21}}^{\rho_{22}} \int_{\rho_{31}}^{\rho_{32}} s_1(0, x_2, x_3, t) dx_2 dx_3 \right] dt \quad (4.10a)$$

where the solute influx, s_1 , is given as:

$$s_1(0, x_2, x_3, t) = -\theta D_{11} \frac{\partial c}{\partial x_1} - u_1 \theta c_0, \quad x_1 = 0, \quad \rho_{21} \leq x_2 \leq \rho_{22}, \quad \rho_{31} \leq x_3 \leq \rho_{32} \quad (4.10b)$$

M_0 was kept the same (0.125kg) for both chemicals. The flow and transport simulations proceeded until a solute breakthrough was completed at a horizontal control plane (CP) located at a depth of 1.5m.

4.2 Results and Discussion

4.2.1 Variability of the Flow

The response of the flow domain in the absence and in the presence of uptake by root

plants is characterized in terms of the profiles of the horizontal averages, the mean,

$\langle p(x_1; t) \rangle$ and the variance, $\langle p'(x_1; t)^2 \rangle$ given by:

$$\langle p(x_1; t) \rangle = (L_2 L_3)^{-1} \int_0^{L_2} \int_0^{L_3} p(x_1, x_2; x_1, t) dx_2 dx_3 \quad (4.11a)$$

$$\langle p'(x_1; t)^2 \rangle = (L_2 L_3)^{-1} \int_0^{L_2} \int_0^{L_3} [p(x_2, x_3; x_1, t) - \langle p(x_1; t) \rangle]^2 dx_2 dx_3 \quad (4.11b)$$

where $p = \theta, \psi, y = \log K, J_i = \partial(-\psi - x_1)/\partial x_i, u_i, i = 1, 2, 3$.

Profiles of the mean, $\langle p(x_1; t) \rangle$ and the standard deviation, $[\langle p'(x_1; t)^2 \rangle]^{1/2}$ of $p(\underline{x})$ are depicted in Figs. 4.2 through 4.6. The profiles in these figures represent different times (denoted by the numbers labeling the various curves) between two successive irrigation events. It is demonstrated in these figures that water application influences the water regime mostly in the upper part of the soil profile. In response to the water application event, both the mean value and the standard deviation of θ and $u_i, i = 1, 2, 3$ increase while those of ψ decrease; on the other hand, the mean values of both $\log K$ and $J_i, i = 1, 2, 3$, increase while their standard deviations decrease. Following the termination of the water application, the mean values and the standard deviations of θ and $u_i, i = 1, 2, 3$ decrease, those of ψ increase, the mean values of both $\log K$ and J_i decrease while the standard deviations of y and $J_i, i = 1, 2, 3$ increase. Note that the mean values and the standard deviations of $p(x_1; t)$ change monotonically with increasing time, in such a way that when the time for a subsequent irrigation event is reached (after 21 days), their profiles are essentially restored to those prevailing just before the previous water application. Note also that the relative variability of each of the entities depicted in Figs. 4.2 through 4.6, expressed in terms of $CV_p(x_1; t) = [\langle p'(x_1; t)^2 \rangle]^{1/2} / \langle p(x_1; t) \rangle$ ($p = \psi, \theta, u_i, J_i, i = 1, 2, 3$), or that of K expressed in terms of

$CV_K(x_1;t) = \{\exp[\langle y'(x_1;t)^2 \rangle] - 1\}^{1/2}$ increases with time as the soil profile dries after the termination of the water application.

The mean values of the transverse components of the head gradient and the velocity vectors, J_i (Fig. 4.5) and u_i (Fig. 4.6), $i=2,3$, respectively, are essentially insensitive to the temporal variations in the water influx at the soil surface. On the other hand, the longitudinal component of the mean head gradient, $\langle J_1 \rangle$ is very sensitive to the temporal variations of the influx at the soil surface. In response to the water application, $\langle J_1 \rangle$ increases considerably in the upper part of the soil profile (Fig. 4.5); it decreases with increasing time following the termination of the water application, and may change its sign in the upper part of the soil profile, as the profile dries. At a sufficiently large vertical distance from the soil surface, however, $\langle J_1 \rangle$ fluctuates about unity. Note that although $\langle J_1 \rangle$ may become negative when the profile dries (Fig. 4.5), $\langle u_1 \rangle$ remains positive (Fig. 4.6). This stems from the highly nonlinear relationships between conductivity and water saturation, and because negative J_1 is associated with relatively low water saturation and, concurrently, very small conductivity. Thus, the contribution of negative $u_1 = K(\theta)J_1/\theta$ values to the mean value of u_1 is very small. Note that the mean value of $\log K$ (Fig. 4.4) is also very sensitive to the flow conditions at the upper boundary and may change by a few orders of magnitude in response to a water application event.

The modulus of the mean velocity vector, $\langle \underline{u} \rangle$, $\langle u \rangle = (\langle u_1 \rangle^2 + \langle u_2 \rangle^2 + \langle u_3 \rangle^2)^{1/2}$, the angle between $\langle \underline{u} \rangle$ and the positive x_1 coordinate, $\chi = \cos^{-1}(\langle u_1 \rangle / \langle u \rangle)$ and the angle between the projection of $\langle \underline{u} \rangle$ on the x_2x_3 plane and the positive x_2 coordinate, $\mu = \tan^{-1}(\langle u_3 \rangle / \langle u_2 \rangle)$ as functions of time between two successive water applications and for selected soil depths, are depicted in Fig. 4.7. This figure clearly demonstrates the temporal fluctuations in both the magnitude and the direction of the mean velocity vector,

particularly in the upper part of the soil profile. Water uptake by roots decreases the periodic, temporal fluctuations in the magnitude of the mean velocity vector, and produces high-frequency temporal fluctuations in the direction of the mean velocity vector, which decrease with increasing soil depth.

The variability in log-unsaturated conductivity (Fig. 4.4) in particular when the profile dries ($\sigma_y^2 = \langle y'(x_1; t)^2 \rangle \geq 5$), is very large compared with the variability in log-saturated conductivity (Table 1). This stems from the constitutive relationships for unsaturated flow ((5)), i.e., decreasing mean water saturation magnifies the contribution of the variability in the pore-size parameters β , n and m (Table 1) and in the capillary pressure head (Fig. 4.3) to the variability in $\log K$ ((5b)). The extremely large $\log K$ variance suggests that the contrast between subdomains of different conductivities is very large, and may lead to a relatively large variability in the head gradient (Fig. 4.5). It is shown in Figs. 4.5 and 4.6 that the transverse components of the head gradient variance and, in particular, those of the velocity variance are not negligibly small compared with their respective longitudinal components. The ratio $\langle u'_i(x_1; t)^2 \rangle / \langle u'_1(x_1; t)^2 \rangle$ ($i=2,3$) which is relatively small just after the water application increases as the soil dries after the termination of the water application and may exceed unity in the presence of water uptake by plant roots (Fig. 4.6).

The pattern of the mean θ , ψ , $\log K$, J_i and u_i , $i=1,2,3$, profiles in Figs. 4.2 through 4.6, respectively, is a direct consequence of the events occurring at the soil-atmosphere interface (irrigation/rain, evapotranspiration) and the subsequent processes occurring in the soil profile (infiltration, redistribution and uptake by plant roots). Their irregular, apparently erratic behavior reflect the heterogeneity in the soil properties. Water uptake by plant roots is shown to produce a drier soil profile with lower conductivity, smaller velocity, steeper head gradients and a smaller travel distance of the wetting front during the infiltration.

The variability in the response of the flow domain, demonstrated by the $\langle p'(x_1;t)^2 \rangle^{1/2}$ profiles in Figs. 4.2 through 4.6 is explained by the fact that during redistribution periods between successive water applications, the response is relaxed from the restraint imposed during the infiltration periods by the spatially uniform, unidirectional vertical influx, and is adjusted to the spatial heterogeneity in the formation properties. Consequently, $CV_p(x_1;t)$ ($p=\theta, \psi, \log K, J_i, u_i, i=1,2,3$) decreases during the infiltration periods and increases with increasing time, following the termination of the water application. Furthermore, during the infiltration periods, the transverse components of the velocity variance are affected more than its longitudinal component, by the restraint imposed by the spatially uniform, unidirectional vertical influx. Consequently, the ratios $\langle u'_i(x_1;t)^2 \rangle / \langle u'_1(x_1;t)^2 \rangle$ ($i=2,3$) decrease during the infiltration periods and increase with increasing time, following the termination of a water application event.

Water uptake by plant roots is shown to increase the relative variability in the response of the flow domain (*i.e.*, in terms of $CV_p(x_1;t)$), to decrease the extent of the flow domain which responds to the water application, to increase the longitudinal component of the head gradient mean and variance, to decrease the longitudinal component of the velocity mean and variance, and to increase the transverse components of the velocity variance relative to its longitudinal component. In other words, water uptake by the plant roots suppresses the high velocities and, consequently, reduces the velocity in the vertical direction and smooths its heterogeneity.

Note that the ratios $\langle u'_i(x_1;t)^2 \rangle / \langle u'_1(x_1;t)^2 \rangle$ ($i=2,3$) (ranging from 0.3 to 1.2) are much larger than their counterparts based on first-order approximation of the velocity covariance in a steady-state, unsaturated flow [Russo, 1995a,b,1997], restricted to log-unsaturated conductivity variance, σ_y^2 , smaller than unity. Using second-order corrections

to the velocity covariance tensor in steady-state, saturated flow, it has been shown [Deng and Cushman, 1995] that the transverse components of the velocity covariance are more sensitive than the longitudinal component, to the second-order correction. Consequently, the ratios $\langle u_i'^2 \rangle / \langle u_1'^2 \rangle$ ($i=2,3$) are expected to increase with increasing σ_y^2 . This may be inferred from Fig. 4.8, i.e., the ratios $\langle u_i'(x_1;t)^2 \rangle / \langle u_1'(x_1;t)^2 \rangle$ ($i=2,3$) increase with time as the soil profile dries and as σ_y^2 increases after the termination of the water application. Water uptake by roots, which enhances the drying of the soil profile and, concurrently, the increase in σ_y^2 (Fig. 4.4) further increases the ratios $\langle u_i'(x_1;t)^2 \rangle / \langle u_1'(x_1;t)^2 \rangle$ ($i=2,3$).

4.2.2 Displacement and Spreading of the Solute Concentration

Solute plumes in the absence of water uptake by plant roots for a passive solute are depicted in Fig. 4.8. This figure displays the surface (using a cutoff of $0.01 \langle c(\underline{x};t) \rangle$) of the plume of the simulated solute resident concentrations, $c(\underline{x},t)$, obtained from the solution of (4.1) subject to (4.8), and the solution of (4.2) subject to (4.9), for two different travel distances, R_1 , defined by (3.1a). The irregular, ostensibly erratic, spatial variation of the plumes demonstrated in Fig. 4.8 is attributed to the small-scale variability in the hydraulic properties of the heterogeneous, unsaturated soil. When the center of mass of the plume has travelled only a few correlation scales of the formation properties in the longitudinal direction ($R'_1 = R_1/I_{f1} = 5$), the plume shows spreading in both the vertical longitudinal and the horizontal transverse directions. As time elapses, and the center of mass of the plume is displaced further ($R'_1 = 10$), the plume evolves further.

Values of the horizontal averages, the mean $\langle c(x_1;t) \rangle$ and the standard deviation, $[\langle c'(x_1;t)^2 \rangle]^{1/2}$ (Fig. 4.9) were obtained by averaging $c(\underline{x};t)$ over a time-dependent horizontal region that traces the lateral spreading of the solute plume. In other words, they

were obtained from (11) with $p=c\theta$ and a denominator given by $\int \int \theta dx_2 dx_3$ instead of $L_2 L_3$, and by using the integration limits $L_{i1}(t)$ and $L_{i2}(t)$ instead of 0 and L_i , $i=2,3$, respectively, where $L_{i1}(t)=\rho_{i1}-2\sqrt{S_{ii}(t)}$, $L_{i2}(t)=\rho_{i2}+2\sqrt{S_{ii}(t)}$, $i=2,3$; $(\rho_{i2}-\rho_{i1})$ $i=2,3$ are the lateral extents of the solute entry zone, and $S_{ii}(t)$ ($i=2,3$) are the respective transverse components of the second spatial moment tensor given by (3.1b).

The mean c profile (Fig. 4.9a,c) is initially asymmetric and later exhibits the symmetrical Fickian distributions typical of the solution of the classical one-component CDE with constant coefficients. The $[<c'(x_1;t)^2>]^{1/2}$ profiles (Fig. 4.9b,d) generally follow the pattern of the $<c(x_1;t)>$ profiles, and increase with depth as the depth of the $<c(x_1;t)>$ peak is approached; $[<c'(x_1;t)^2>]^{1/2}$ then decreases with increasing depth at soil depths below the $<c(x_1;t)>$ peak. Note that $[<c'(x_1;t)^2>]^{1/2}$ vanishes when $x_1 \rightarrow 0$, and when $x_1 \rightarrow \infty$, where $<c(x_1;t)> \rightarrow 0$. The profiles of Figs. 4.9a,c and 9b,d suggest that the relative variability of the solution concentration in terms of $CV=[<c'(x_1;t)^2>]^{1/2}/<c(x_1;t)>$, may be very large at the fringe of the solute body, since $<c(x_1;t)> \rightarrow 0$ faster than $[<c'(x_1;t)^2>]^{1/2}$.

Water uptake by plant roots is shown to decrease the spreading of $<c(x_1;t)>$ in the vertical direction and, concurrently, to delay its dilution, and to reduce the skewness of both the mean and the standard deviation concentration profiles (Fig. 4.9). This is because water uptake by the plant roots eliminates the high velocities and, consequently, reduces the vertical velocity and smooths its heterogeneity (Fig. 4.6). On the other hand, sorption is shown to increase the spreading of $<c(x_1;t)>$ in the longitudinal direction and, concurrently, to expedite its dilution, and to increase the skewness of both the mean and the standard deviation concentration profiles (Fig. 4.9). This result stems from the negative cross-correlation between $\log K_d$ and $\log K_s$ assumed in the present study, in agreement with the theoretical results of Bellin et al. [1993] and Russo [1996a] for steady, saturated and

unsaturated flows, respectively.

4.2.3 Spatial Moments of the Solute Plume

It is clear from Fig. 4.9 that concentration point values are subject to large uncertainty, attributed to the complex heterogeneity of the formation hydraulic properties and, therefore, the prediction of concentration point values is error prone. Consequently, we focus our attention on larger-scale, integrated measures of the solute transport, such as the spatial moments of the distribution of the point values of c . In turn, these moments are subject to a much lesser degree of uncertainty than are the point values. The first two spatial moments of the distribution of c are given by (3.1) where the zeroth-moment of the spatial distribution of c , the total mass of the solute, M is constant given by $M = \int \theta(\underline{x})c(\underline{x},t)d\underline{x}$, $\underline{R}(t) = (R_1, R_2, R_3)$ is the coordinate of the centroid of the solute plume, and $S'_{ij}(t)$ ($i, j = 1, 2, 3$) are second spatial moments, proportional to the moments of inertia of the plume. Note that under ergodic conditions for the spatial moments, assumed to prevail if the lateral extent of the entry zone is large enough as compared with the scale of the formation heterogeneity in the horizontal direction, $S_{ij}(t) = S'_{ij}(t) - S'_{ij}(0) \approx X_{ij}(t, 0)$. Hence, under these conditions, the spatial moments of the solute body can be characterized by the one-particle-trajectory statistical moments, $X_{ij}(t; 0)$ ($i, j = 1, 2, 3$).

The dependence of the longitudinal, R_1 , and transverse, R_i ($i = 2, 3$) components of the coordinate of the centroid of the solute plume, $\underline{R}$, upon travel time, t is depicted in Fig. 4.10. As expected, the center of mass is displaced vertically in the direction of the mean flow, in a manner which is related to the temporal behavior of the net applied water (Fig. 4.1b). In the horizontal plane, perpendicular to the direction of the mean flow, R_2 and R_3 essentially remain constant with time. The time fluctuations in R_1 (Fig. 4.10), originating

from the recharge cycles at the inlet zone, are smoothed out as time elapses and the center of mass of the plume is displaced to a sufficiently large distance from the inlet zone. As expected, both sorption and water uptake by roots are shown to retard the displacement of the plume in the longitudinal (vertical) direction.

Estimated values of the longitudinal, S_{11} and the transverse, S_{ii} ($i=2,3$) components of the spatial covariance tensor, $S_{ij}(t)=S'_{ij}(t)-S'_{ij}(0)$ ($i,j=1,2,3$) as functions of the travel distance of the center of mass, R_1 , are given in Fig. 4.11. Since the spatial covariance of the solute distribution is a measure of the spreading of the distribution about its center of mass, the changes in the covariance structure with travel distance may reflect the changes of the concentration distribution that occur because of the heterogeneity induced in the solute velocity field by small-scale heterogeneity in the soil hydraulic properties.

The longitudinal component, S_{11} depicted in Fig. 4.11, generally describes a transport process which is initially controlled by convection only (i.e., S_{11} is initially proportional to the square of the travel distance), and then continuously changed to a convection-dispersion transport process (for which S_{11} increases linearly with travel distance). The fluctuations in S_{11} stem from the temporal variations in the flow conditions at the soil surface, and are generally related to the temporal variations in the net applied water (Fig. 4.1b), and the resultant fluctuations in the downward displacement of the center of mass (Fig. 10). The transverse components, S_{22} and S_{33} , fluctuate only slightly in time and do not approach the constant asymptotic values, which, in turn, are characteristics of the convection-dispersion transport process, when the mean head gradient coincides with the vertical axis [Dagan, 1989]. Instead, the evolution of S_{22} and S_{33} at a rate faster than linearly in R_1 , persists over longer travel distances, and their magnitudes are only slightly smaller than that of S_{11} . This result stems from the periodic, transient nature of the flow, and the multidimensionality of

its variation (Figs. 4.5 and 4.6). The small disparity between the magnitudes of the vertical and the horizontal components of the velocity variance is shown to increase the lateral mixing of the solute, effectively smoothing out the extremes in solute convection, to slow down the plume spreading in the longitudinal direction and, at the same time, to increase its spreading in the transverse directions (Fig. 4.11).

The relatively large values of the ratios S_{ii}/S_{11} , $i=2,3$ are in qualitative agreement with the results of the first-order analyses of transport under steady-state unsaturated flow [Russo, 1995b] and quasi-steady-state saturated flow [Zhang and Neuman, 1996]. Results of the former analysis reveal that, as the angle between the mean velocity vector $\langle \underline{u} \rangle$ and the x_1 axis increases, the longitudinal component of the displacement covariance tensor, $X(t)$, $X_{11}(t)$ decreases, and it evolves at a rate faster than linearly in t for shorter travel times. The converse is true for the transverse components of $X(t)$, $X_{ii}(t)$ ($i=2,3$), which also increase with increasing angle between $\langle \underline{u} \rangle$ and the x_j axis, $j=3,2$. The results of the latter analysis reveal that while periodic temporal fluctuations in the magnitude of the mean velocity may either enhance or reduce solute spreading, periodic temporal fluctuations in the direction of the mean velocity cause $X_{11}(t)$ to decrease and $X_{ii}(t)$ ($i=2,3$) to increase. Nevertheless, the ratios S_{ii}/S_{11} ($i=2,3$) in Fig. 4.11, are much larger than those expected based on the aforementioned first-order analyses of transport under steady-state unsaturated flow, or quasi-steady-state saturated flow.

Sorption is shown to increase both the magnitude of S_{11} and the travel distance for which it evolves at a rate faster than linearly in R_1 , but essentially has no effect on the magnitude of S_{ii} ($i=2,3$), in qualitative agreement with the results of the first-order analyses of transport of sorptive solute under steady-state unsaturated flow [Russo, 1996a]. On the other hand, water uptake by plant roots (with larger spatial variations in the transverse components of

the velocity vector (Fig. 4.6) and smaller periodic temporal fluctuations in the magnitude of the mean velocity vector, but with a larger, high-frequency, temporal fluctuations in the direction of the mean velocity vector (Fig. 4.6), is shown to decrease the magnitude of S_{11} , to increase the travel distance over which it evolves at a rate faster than linearly in R_1 , and to increase the ratios S_{ii}/S_{11} ($i=2,3$).

4.2.4 Effective Retardation Factor

The ratio between the longitudinal components of the effective solute velocity vector, $\underline{V}$, defined as the time rate of change of the displacement of the center of mass

$$\underline{V}(t) = [dR_1/dt, dR_2/dt, dR_3/dt]^T \quad (4.12)$$

associated with the passive and the sorptive solutes, can be used to define an effective retardation factor, $R_f(t)$ [Burr et al., 1994]. Because of the time fluctuations in $V_1(t)$, however, the ratio between travel distances, $R_1(t) = \int_0^t V_1(t') dt'$ associated with the passive (p) and the sorptive (s) solutes, was used to calculate an effective retardation factor, $R_f(t) = R_1^p(t)/R_1^s(t)$, which accounts for the cumulative retardation effects of the formation along the path of migration. The time fluctuations in the values of $R_f(t)$ depicted in Fig. 4.12 are related to the recharge cycles at the inlet zone. $R_f(t)$ initially increases rapidly with increasing time, and later increases more slowly with increasing time. In the case of water uptake by plant roots, for which values of $R_f(t)$ are available for a longer elapsed time, after the fast increase in $R_f(t)$ with increasing time, $R_f(t)$ slightly decreases with increasing time, and essentially approaches constant asymptotic values eventually. The effective retardation factors depicted in Fig. 4.12 suggest that spatial variations in both the chemical and the physical properties of the formation can impart a pseudokinetic behavior to the large-scale

sorption, even though the underlying local-scale sorption is an equilibrium process. This behavior of $R_f(t)$ (Fig. 4.12) is a result of the transient nature of the flow in the upper part of the soil profile; this, in turn, magnifies the effect on the flow, of the spatial variability in the physical properties of the formation. At a sufficiently large vertical distance from the soil surface, however, where the flow is free of the constraints imposed by the conditions at the soil surface, R_f approaches its asymptotic constant value. Water uptake by plant roots, which has been shown to decrease the impact of the physical heterogeneity of the formation on the velocity (Fig. 4.6), decreases the effective retardation factor.

The pseudokinetic behavior of $R_f(t)$ (Fig. 4.12) is in contrast with the time-invariant R_f calculated by Burr et al. [1994] and Yang et al. [1996] for transport under steady-state, three-dimensional saturated, and two-dimensional unsaturated flows, respectively. The pseudokinetic behavior of $R_f(t)$ (Fig. 4.12) is, however, in agreement with the behavior of R_f as calculated by Roberts et al. [1986] from the Borden PCE plume data obtained under natural, transient, saturated-flow conditions. Note, however, that the characteristic time scale of the pseudokinetic behavior of R_f in the Borden site was much larger than those of $R_f(t)$ depicted in Fig. 4.12.

4.2.5 Solute Breakthrough and Travel Time PDF

Solute breakthrough is calculated from the flux-averaged concentration, c_f , defined [Kreft and Zuber, 1978] by $c_f = \int \underline{s} \cdot \underline{v} dA / \int \theta \underline{u} \cdot \underline{v} dA$, where $\underline{s}$ and $\underline{u}$ are the solute flux and the velocity vectors, respectively, with $s = \underline{s} \cdot \underline{v}$ and $\theta u = \theta \underline{u} \cdot \underline{v}$ being the mass of solute and the volume of water per unit time and unit area moving through a surface element of unit normal $\underline{v}$, and water saturation, θ and the integration is over a planar area A . Mean and standard deviation of the solute breakthrough curve (BTC), evaluated by averaging c_f over each of two

horizontal control planes (CP) located at two different vertical distances L from the inlet zone at the soil surface, are depicted in Figs. 4.13 and 4.14, respectively, in terms of the dimensionless variables, $T=R_1(t)/L$, $\langle C(T;L) \rangle = \langle c_f(T;L) \rangle / \int_0^\infty \langle c_f(T;L) \rangle dT$ and $[\langle C'(T;L)^2 \rangle]^{1/2} = [\langle c_f'(T;L)^2 \rangle]^{1/2} / \int_0^\infty \langle c_f(T;L) \rangle dT$.

In general, the expected BTCs (Fig. 4.13) exhibit skewness that is characterized by an earlier breakthrough, by an enhanced peak arrival, and by a longer tailing. The skewness of the expected BTCs, however, decreases with increasing distance to the CP. Sorption, which in the case of negatively correlated $\log K_s$ and $\log K_d$ adds to the variability of the solute velocity, is shown to increase the skewing of the solute pulse, in qualitative agreement with the results of the first-order analyses of transport of sorptive solute under steady-state unsaturated flow [Russo, 1996b]. On the other hand, water uptake by roots, which restrained the variability in the water velocity and, concurrently, in the solute velocity, is shown to decrease the skewing of the solute pulse.

The BTC standard deviations (Fig. 4.14), particularly those which were evaluated at the shallower CP, are much more sensitive to the temporal, transient flow conditions at the soil surface, than the mean BTCs. Consequently, they exhibit substantial, high-frequency, temporal fluctuations. Furthermore, they exhibit skewness, with tailing much longer than those of the respective expected BTCs (Fig. 4.13). The BTC standard deviations increase with scaled travel time, T , as the $\langle C(T;L) \rangle$ peak is approached, and decrease at T beyond the $\langle C(T;L) \rangle$ peak. Note that $[\langle C'(T;L)^2 \rangle]^{1/2}$ must vanish when $T \rightarrow 0$, and when $T \rightarrow \infty$, in which $\langle C(T;L) \rangle \rightarrow 0$. Comparison of the profiles of Figs. 4.13 and 4.14, suggests that the uncertainty in the expected BTCs, expressed as $CV = [\langle C'(T;L)^2 \rangle]^{1/2} / \langle C(T;L) \rangle$, is relatively large around the first arrival time, and decreases with increasing T , reaches a minimum in the vicinity of the $\langle C(T;L) \rangle$ peaks, and increases with increasing T as T

increases further, since $\langle C(T;L) \rangle \rightarrow 0$ much faster than $[\langle C'(T;L)^2 \rangle]^{1/2}$. Comparison of Fig. 4.13 and Fig. 4.14 suggests that both sorption and water uptake by plant roots increase the uncertainty in the predicted BTC.

The mean normalized BTCs (Fig. 4.13) corresponding to a narrow-pulse input of solute, can be used as an approximation of the one-particle travel time PDF, $g_1(T;L)$. The goodness of fit of specific process representations of $g_1(T;L)$, to the simulated $g_1(T;L)$ may, therefore, be used in order to identify the process controlling the mean BTCs in Fig. 4.13. Two plausible PDFs for travel time, *i.e.*, Fickian and lognormal PDFs, are considered here. The former is the PDF for one-particle travel time associated with the classical convection-dispersion equation (CDE), representing a transport whose travel-time variance grows linearly with travel distance. The latter travel-time PDF is associated with the convective lognormal transfer function model (CLT) of Jury [1982], representing transport whose travel-time variance increases quadratically with travel distance. Employing the method of moments, the parameters of the one-dimensional vertical Fickian PDF ($V^* = u_1/R_f$ and $D^* = D_{11}/R_f$) and of the lognormal PDF (μ and σ^2) are given [Jury and Sposito, 1985] as:

$$V^* = L/T_1 \quad (4.13a)$$

$$D^* = L^2 T_1^3 / 2(T_2 - T_1^2)$$

and

$$\mu = (4 \log T_1 - \log T_2) / 2 \quad (4.13b)$$

$$\sigma^2 = \log T_2 - 2 \log T_1$$

where T_1 and T_2 are the first two normalized travel time moments of the horizontally-averaged flux concentration given as

$$T_N(L) = \int_0^{\infty} t^N \langle c_f(t;L) \rangle dt / \int_0^{\infty} \langle c_f(t;L) \rangle dt, \quad N=1,2 \quad (4.14)$$

The normalized PDF for one-particle travel time, $g_1 L/V_1$ calculated from the simulated flux concentrations and the fitted PDFs are depicted in Fig. 4.15 for CPs located at two different vertical distances, L . As expected, [e.g., Jury and Sposito, 1985], for a given L , the two different PDFs provide essentially the same fit to the simulated travel time PDF when their parameters are optimized at the same travel distance ($L=0.75\text{m}$, Fig. 4.15a-d). Both PDFs exhibit skewing that is consistent with the skewing in the simulated travel time PDF, but are characterized, however, by a slightly earlier breakthrough and by a smaller peak than those of the simulated travel time PDFs, especially when water uptake by roots is considered. For a given CP located at a longer travel distance ($L=1.5\text{m}$, Fig. 4.15e-h), however, the disparity between the two different PDFs (with parameters optimized at $L=0.75\text{m}$) is substantial. At $L=1.5\text{m}$, the lognormal PDF is much more skewed than the Fickian PDF, that, in turn, provides a relatively good fit to the simulated PDF at this travel distance. This suggests that the transport of both passive and sorptive solutes, within the root zone and below the root zone, may be approximately described by the CDE with constant, effective coefficients. In other words, the periodic, transient-flow regime, and the multidimensionality of its variation (Figs. 4.5 and 4.6) enhance the lateral dispersion of the solute, that, in turn, promotes mixing between regions of differing convection, and leads to an approximately Fickian behavior.

4.3 Concluding Remarks

The main purpose of the present study was to investigate field-scale transport of both tracer and reactive (sorptive) solutes under realistic field conditions in a three-dimensional, heterogeneous, partially saturated soil. The results of this investigation are represented in Figs. 4.2 through 4.15. The main findings presented in the present Chapter may be summarized as follows:

- (i) The pattern of water saturation, capillary pressure, conductivity and head gradient fields, the resultant velocity fields, and, consequently, the spreading and the breakthrough of the solute pulse, are considerably affected by the spatial heterogeneity in the soil properties and the boundary conditions imposed on the flow in the entry zone at the soil surface.
- (ii) Under realistic boundary conditions at the soil surface (i.e., periodic water application, in which the time between two successive applications is much longer than the application time), the relative variability in the velocity field is restrained during the infiltration periods and enhanced during the redistribution periods. The resultant spatial fluctuations in the resultant velocity field are three-dimensional with substantial transverse components, which promote lateral mixing of the solute, smooth out the extremes in solute convection, slow down the longitudinal spreading and increase the transverse spreading of the solute plume, and reduce the skewing of the solute breakthrough. The periodic influx may produce periodic temporal fluctuations in both the magnitude and the direction of the mean velocity vector, which, in turn, further enhance transverse spreading of the solute.
- (iii) Water uptake by the plant roots is shown to produce a drier soil profile, with smaller conductivity and steeper head gradients. Consequently, it slows down the solute velocity in the vertical direction and smooths its spatial heterogeneity, and further diminishes the longitudinal spreading of the solute plume and the skewing of the solute breakthrough.

(iv) Sorption reduces the solute velocity in the vertical direction. For the physically plausible situation in which $\log K_d$ is negatively correlated with $\log K_s$, sorption contributes to the heterogeneity in the solute velocity and increases both the longitudinal spreading of the solute plume and the skewing of the solute breakthrough.

(v) For both the passive and the sorptive solutes, the periodic, transient flow regime and the multidimensionality of its variation enhance lateral dispersion of the solute, the magnitude of which is much larger than the one expected on the basis of first-order theories of transport under steady-state, unsaturated flow. The enhanced lateral dispersion promotes mixing between regions of differing convection, and leads to an approximately Fickian behavior of the transport within and below the root zone.

(vi) Spatial variations in both the chemical and the physical properties of the formation can impart a pseudokinetic behavior to the large-scale sorption, even though the underlying local-scale sorption is an equilibrium process. This stems from the transient nature of the flow in the upper part of the soil profile that, in turn, magnifies the effect on the flow, of the spatial variability in the physical properties of the formation.

Before concluding, we would like to stress that the numerical experiment conducted in the present study is a powerful tool that may provide much more detailed information about the effects of spatial variability in soil properties on the response of the flow system, than is attainable in practice from field investigations. We would like to emphasize, however, that the conclusions drawn from this study should be considered with caution, inasmuch as the numerical results presented in this study are based on analyses of single realizations of both formation properties and flow- and transport-attributed entities, and are restricted by a few limiting assumptions.

Appendix A: Derivation of the Velocity Covariance Tensor (1.13)

Considering the transformations,

$$e_{p2}=I_{p2}/I_{p1}, e_{p3}=I_{p3}/I_{p1}, k'_{pi}=k_i I_{pi}, dk'_p=I_{p1}I_{p2}I_{p3}dk, \xi'_{pi}=\xi_i/I_{pi} \quad (A1)$$

where k_i and I_{pi} , $i=1,2,3$ are the i -th components of the wave number vector and the correlation scale vector of p , respectively, and $p=1,2,3$ for f , a and fa , respectively.

Substituting (A1) in the spectrum (1.12), the Fourier transform of the resultant is:

$$u_{ij}(\xi; \Theta) = U^2 \sum_{p=1}^3 \frac{c_p \sigma_p^2}{\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d_{ij}^p \exp(j \underline{k}'_p \cdot \underline{\xi}'_p) d\underline{k}'_p}{(1 + \underline{k}'_p{}^2)^2} \quad (A2)$$

where

$$\begin{aligned} d_{11}^p &= (1 - \frac{k'^2_{p1}}{K_p^2})^2 \\ d_{22}^p &= \frac{k'^2_{p1} k'^2_{p2}}{K_p^2} \\ d_{33}^p &= \frac{k'^2_{p1} k'^2_{p3}}{K_p^2} \\ d_{12}^p &= d_{21}^p = \frac{(k'^3_{p1} k'_{p2} - K_p^2 k'_{p1} k'_{p2})}{K_p^2} \\ d_{13}^p &= d_{31}^p = \frac{(k'^3_{p1} k'_{p3} - K_p^2 k'_{p1} k'_{p3})}{K_p^2} \\ d_{23}^p &= d_{32}^p = \frac{k'^2_{p1} k'_{p2} k'_{p3}}{K_p^2} \end{aligned} \quad (A3)$$

$g_p=(2J_1-1)A I_{p1}$ and j is the imaginary unit.

$$K_p^2 = [j g_p k'_{p1} + k'^2_{p1} + (k'^2_{p2}/e_{p2}^2) + (k'^2_{p3}/e_{p3}^2)]^2$$

To simplify (A2), the wave number vector, $\underline{k}'_p$ is expressed in terms of the spherical coordinates system (k'_p, ϕ, μ) , i.e.,

$$\begin{aligned} k'^2_{p1} &= k'^2_p \cos^2 \phi \\ k'^2_{p2} &= k'^2_p \sin^2 \phi \cos^2 \mu, \quad p=1,2,3 \\ k'^2_{p3} &= k'^2_p \sin^2 \phi \sin^2 \mu \end{aligned} \quad (A4)$$

and

$$d\underline{k}'_p = \sin \phi \, d\phi \, d\mu \, dk'_p \quad (A5)$$

where ϕ is the angle between $\underline{k}'_p$ and the k'_{p1} coordinate, μ is the angle between the projection of $\underline{k}'_p$ on the $k'_{p2}k'_{p3}$ plane and the k'_{p2} coordinate, and $k'_p = |\underline{k}'_p|$. Similarly, the scaled separation vector, $\underline{\xi}'_p$, is also expressed in terms of the spherical coordinates system (ξ'_p, χ, θ) , i.e.,

$$\begin{aligned} \xi'^2_{p1} &= \xi'^2_p \cos^2 \chi \\ \xi'^2_{p2} &= \xi'^2_p \sin^2 \chi \cos^2 \theta, \quad p=1,2,3 \\ \xi'^2_{p3} &= \xi'^2_p \sin^2 \chi \sin^2 \theta \end{aligned} \quad (A6)$$

where χ is the angle between $\underline{\xi}'_p$ and the ξ'_{p1} coordinate, θ is the angle between the projection of $\underline{\xi}'_p$ on the $\xi'_{p2}\xi'_{p3}$ plane and the ξ'_{p2} coordinate, and $\xi'_p = |\underline{\xi}'_p|$. Coordinates of the scaled separation vector (A6) are superimposed on the coordinates of the wave number vector (A4) in such a way that the ξ'_{p1} coordinate coincides with the k'_{p1} coordinate, with ν_p , the angle between $\underline{\xi}'_p$ and $\underline{k}'_p$, (see Fig. 1.1a) given by:

$$\nu_p = \cos^{-1}[\cos\chi \cos\phi + e_p(\sin\chi \cos\theta \sin\phi \cos\mu + \sin\chi \sin\theta \sin\phi \sin\mu)] \quad (A7)$$

where $p=1$ to 3. Further simplification is gained by substitution of the scalar product,

$\underline{k}'_p \cdot \underline{\xi}'_p = k'_p \xi'_p \cos\nu_p$, in the trigonometric expansion of the exponential function in (A2):

$$\exp(j\underline{k}'_p \cdot \underline{\xi}'_p) = \cos(k'_p \xi'_p r_p) + j\sin(k'_p \xi'_p r_p) \quad (A8)$$

where $r_p = \cos\nu_p$, and $p=1,2,3$. Finally, for heterogeneous porous formations of axisymmetric anisotropy, with mean flow in the vertical direction, perpendicular to the formation bedding, we have:

$$I_{p2} = I_{p3} = I_{ph}, \quad I_{p1} = I_{pv}, \quad e_{p2} = e_{p3} = 1/e_p, \quad e_p = I_{pv}/I_{ph} \quad p=1,2,3 \quad (A9)$$

$$e_p^{-2} k_{p1}'^2 + k_{p2}'^2 + k_{p3}'^2 = k'^2 (e_p^{-2} \cos^2\phi + \sin^2\phi)$$

Substituting (A3), (A4), (A5), (A8) and (A9) in (A2), we have:

$$u_{ij}(\xi, \theta, \chi; \Theta) = U^2 \sum_{p=1}^3 \frac{c_p \sigma_p^2}{\pi^2} \int_0^\infty \int_0^{2\pi} \int_0^\pi c_{ij}^p [\cos(k'_p |r_p| \xi'_p) + j \sin(k'_p |r_p| \xi'_p)] b_p^2 \sin\phi d\phi d\mu dk'_p \quad (A10)$$

where the c_{ij}^p terms are given by:

$$\begin{aligned} c_{11}^p &= (1 - \cos^2\phi)^2 \\ c_{22}^p &= e_p^{-2} \cos^2\phi \sin^2\phi \cos^2\mu \\ c_{33}^p &= e_p^{-2} \cos^2\phi \sin^2\phi \sin^2\mu \\ c_{12}^p &= c_{21}^p = e_p^{-3} \cos^3\phi \cos\mu - \sqrt{b^2} e_p^{-1} \cos\phi \cos\mu \end{aligned} \quad (A11)$$

$$c_{13}^p = c_{31}^p = e_p^{-3} \cos^3 \phi \sin \mu - \sqrt{b_p^2} e_p^{-1} \cos \phi \sin \mu$$

$$c_{23}^p = c_{32}^p = e_p^{-2} \cos^2 \phi \sin^2 \phi \sin \beta \cos \mu$$

and b_p^2 is given by:

$$b_p^2 = \frac{k_p'^4}{(1+k_p'^2)^2 [k_p'^2 (\sin^2 \phi + e_p^{-2} \cos^2 \phi)^2 + e_p^{-4} \cos^2 \phi g_p'^2]} \quad (A12)$$

The integrand of the imaginary part of (A10) vanishes when integrated with respect to ϕ over the interval $\{0, \pi\}$. Integrating the real part of (A10) with respect to k_p' , the Fourier transform of the spectrum (1.12) is given by (1.13).

Appendix B: Evaluation of $E_{ij}(\xi; \Theta)$ ((2.6))

Our goal here is to evaluate the covariance $E_{ij}(\xi; \Theta)$ ($i, j=1, 2, 3$) given by:

$$E_{ij}(\xi; \Theta) = -\frac{1}{J_i} \frac{\partial C_{yh}(\xi; \Theta)}{\partial \xi_i} + \frac{1}{J_j} \frac{\partial C_{yh}(-\xi; \Theta)}{\partial \xi_j} \quad (B1)$$

Using the first-order approximation for the relationship among the Fourier amplitudes of the perturbations f , a and h [Yeh et al., 1985a], assuming that the mean gradient exists only in the x_1 direction, i.e., $\underline{J} = (J_1, 0, 0)$, and that the correlation scales of $\log K_s$ and α are identical, i.e., $I_y = I_f = I_a$, the spectrum of $E_{ij}(\xi; \Theta)$ ($i, j=1, 2, 3$) is:

$$\hat{E}_{ij}(k; \Theta) = -\frac{2J_1 [\sigma_f^2 + H(\Theta)^2 \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2] I_{y1} I_{y2} I_{y3}}{\pi^2 (1 + I_{y1}^2 k_1^2 + I_{y2}^2 k_2^2 + I_{y3}^2 k_3^2)^2} \frac{k^2 k_i k_j}{(k^2 + j' B k_1)^2} \quad (B2)$$

where $B = (2J_1 - 1)A$ and j' is the imaginary unit.

For heterogeneous porous formations of axisymmetric anisotropy, with mean flow in the

vertical direction, perpendicular to the bedding, i.e., $I_{y1}=I_{yv}$ and $I_{y2}=I_{y3}=I_{yh}$, if the scaled wave number vector $\underline{k}' = \underline{k} I_y$ and the scaled separation vector $\underline{\xi}' = \underline{\xi}/I_y$ are expressed in their spherical coordinates (k', ϕ, μ) and (ξ', χ, θ) , respectively, where $k' = |\underline{k}'|$ and $\xi' = |\underline{\xi}'|$, the Fourier transform of the spectrum $\hat{E}_{ij}(\underline{k}; \Theta)$ ($i, j=1,2,3$) is given by

$$E_{ij}(\underline{\xi}; \Theta) = - \frac{J_1 [\sigma_f^2 + H(\theta)^2 \sigma_a^2 - 2H(\theta) \sigma_{fa}^2]}{2\pi} \int_0^{2\pi} \int_0^\pi \frac{a c_{ij}}{b^2} \sin \phi d\phi d\mu \quad (B3)$$

where a , b^2 and the c_{ij} ($i, j=1,2,3$) terms are given by (1.13b), (1.13c) and (A11), respectively.

Appendix C: Evaluation of G'_{ij} ((2.9)) and G''_{ij} ((2.10))

The tensors G'_{ij} and G''_{ij} ($i, j=1,2,3$) are obtained by integration of $E'_{ij}(\underline{\xi})$ along lines parallel to the mean gradient of unit vector $\underline{U}^R/|\underline{U}^R|$. Here $E'_{ij}(\underline{\xi}) = E_{ij}(\underline{\xi}; \Theta) / \{J_1 [\sigma_f^2 + H^2(\Theta) \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2]\}$, and $E_{ij}(\underline{\xi}; \Theta)$ ($i, j=1,2,3$) is given by (B1). The tensor G'_{ij} is given by

$$G'_{ij}(t) = \int_0^t \int_0^t E'_{ij}(\underline{U}^R \tau', \underline{U}^R \tau'') d\tau' d\tau'' \quad (C1)$$

Assuming that the mean gradient exists only in the x_1 direction, i.e., $\underline{J} = (J_1, 0, 0)$, and that the correlation scales of $\log K_s$ and α are identical, i.e., $I_y = I_f = I_a$, for heterogeneous formations of axisymmetric anisotropy with mean flow in the vertical direction, perpendicular to the bedding, i.e., $I_{y1}=I_{yv}$ and $I_{y2}=I_{y3}=I_{yh}$, $E_{ij}(\underline{\xi}; \Theta)$ ($i, j=1,2,3$) is given by (B3). Using $\underline{\xi} = \underline{U}^R t$ in (B3), dividing by $J_1 [\sigma_f^2 + H^2(\Theta) \sigma_a^2 - 2H(\Theta) \sigma_{fa}^2]$ and substituting the resultant in (C1) employing the Cauchy algorithm, G'_{ij} ($i, j=1,2,3$) is given by

where $t' = tU/RI_{yv}$, a' , b^2 and the c_{ij} ($i, j=1,2,3$) terms are given by (1.19b), (1.13c) and

$$G'_{ij}(t') = -\frac{1}{2\pi} \int_0^{2\pi} \int_0^\pi \frac{a' c_{ij}}{b^2} \sin\phi d\phi d\mu \quad (C2)$$

(A11), respectively.

In a similar way, $G''_{ij}(t) = (1/2)(dG'_{ij}(t)/dt)$ ($i, j = 1, 2, 3$) ((2.10)) is given by

$$G''_{ij}(t) = \int_0^t E_{ij}(\underline{U}^R \tau) d\tau \quad (C3)$$

Using $\xi = U^R t$ in (B3), dividing by $J_1[\sigma_f^2 + H^2(\Theta)\sigma_a^2 - 2H(\Theta)\sigma_{fa}^2]$ and substituting the resultant in (C3), G''_{ij} ($i, j = 1, 2, 3$) is given by

$$G''_{ij}(t') = -\frac{1}{2\pi} \int_0^{2\pi} \int_0^\pi \frac{a'' c_{ij}}{b^2} \sin\phi d\phi d\mu \quad (C4)$$

where a'' is given by (1.20b).

Appendix D: Finite Difference Approximation of the Governing Equations ((4.1) and 4.2))

A flow domain in a Cartesian coordinate system (x, y, z), where z is directed vertically downwards is considered here. The domain is discretized to rectangular cells, measuring Δx , Δy and Δz in the x , y and z directions, respectively. The "mixed" form of Richards equation governing 3-D water flow ((4.1)) is approximated by the fully implicit Euler scheme:

$$\frac{\theta(\psi_{i,j,k}^{n+1}) - \theta(\psi_{i,j,k}^n)}{\Delta t} = \Delta_x(a^{n+1}\Delta_x\psi^{n+1}) + \Delta_y(a^{n+1}\Delta_y\psi^{n+1}) + \quad (D1)$$

$$\Delta_z(a^{n+1}\Delta_z\psi^{n+1}) - \Delta_z(g^{n+1}) - S_{wij,j,k}^{n+1}$$

$$\begin{aligned} \Delta_x(a^{n+1}\Delta_x\psi^{n+1}) = & [a_{i+1/2,j,k}^{n+1}(\psi_{i+1,j,k}^{n+1} - \psi_{i,j,k}^{n+1})/\Delta x_{i+1/2,j,k} \\ & - a_{i-1/2,j,k}^{n+1}(\psi_{i,j,k}^{n+1} - \psi_{i-1,j,k}^{n+1})/\Delta x_{i-1/2,j,k}]/\Delta x_{i,j,k} \end{aligned}$$

$$\begin{aligned} \Delta_y(a^{n+1}\Delta_y\psi^{n+1}) = & [a_{i,j+1/2,k}^{n+1}(\psi_{i,j+1,k}^{n+1} - \psi_{i,j,k}^{n+1})/\Delta y_{i,j+1/2,k} \\ & - a_{i,j-1/2,k}^{n+1}(\psi_{i,j,k}^{n+1} - \psi_{i,j-1,k}^{n+1})/\Delta y_{i,j-1/2,k}]/\Delta y_{i,j,k} \end{aligned}$$

$$\begin{aligned} \Delta_z(a^{n+1}\Delta_z\psi^{n+1}) = & [a_{i,j,k+1/2}^{n+1}(\psi_{i,j,k+1}^{n+1} - \psi_{i,j,k}^{n+1})/\Delta z_{i,j,k+1/2} \\ & - a_{i,j,k-1/2}^{n+1}(\psi_{i,j,k}^{n+1} - \psi_{i,j,k-1}^{n+1})/\Delta z_{i,j,k-1/2}]/\Delta z_{i,j,k} \end{aligned}$$

$$\Delta_z(g^{n+1}) = (g_{i,j,k+1/2}^{n+1} - g_{i,j,k-1/2}^{n+1})/\Delta z_{i,j,k}$$

$\Delta x_{i+1/2,j,k}$, $\Delta y_{i,j+1/2,k}$ and $\Delta z_{i,j,k+1/2}$ are the spacing between the nodes centered at cells (i,j,k) and (i+1,j,k), (i,j,k) and (i,j+1,k), and cells (i,j,k) and (i,j,k+1), respectively; $\Delta x_{i,j,k} = 0.5(\Delta x_{i+1/2,j,k} + \Delta x_{i-1/2,j,k})$; $\Delta y_{i,j,k} = 0.5(\Delta y_{i,j+1/2,k} + \Delta y_{i,j-1/2,k})$; $\Delta z_{i,j,k} = 0.5(\Delta z_{i,j,k+1/2} + \Delta z_{i,j,k-1/2})$. $a_{i\pm 1/2,j,k}^{n+1} = K_{si\pm 1/2,j,k} K_{ri\pm 1/2,j,k}^{n+1}$; $a_{i,j\pm 1/2,k}^{n+1} = K_{si,j\pm 1/2,k} K_{ri,j\pm 1/2,k}^{n+1}$; $a_{i,j,k\pm 1/2}^{n+1} = K_{si,j,k\pm 1/2} K_{ri,j,k\pm 1/2}^{n+1}$; and $g_{i,j,k\pm 1/2}^{n+1} = K_{si,j,k\pm 1/2} k_{ri,j,k\pm 1/2}^{n+1}$ are the interblock conductivities associated with capillary and gravity components of water fluxes, respectively; $K_{si\pm 1/2,j,k}$, $K_{si,j\pm 1/2,k}$ and $K_{si,j,k\pm 1/2}$ are interblock saturated conductivities of the porous medium; $K_{ri\pm 1/2,j,k}^{n+1}$, $K_{ri,j\pm 1/2,k}^{n+1}$ and $K_{ri,j,k\pm 1/2}^{n+1}$ are relative interblock conductivities for the capillary flow component; $k_{ri,j,k\pm 1/2}^{n+1}$ are relative interblock conductivities associated with the gravity component of the vertical flux; and superscripts n and n+1 denote time levels.

$K_{si\pm 1/2,j,k}$, $K_{si,j\pm 1/2,k}$ and $K_{si,j,k\pm 1/2}$ are calculated as harmonic mean values of adjacent

cells [e.g., Bear, 1979], while $K^{n+1}_{ri\pm 1/2,j,k}$, $K^{n+1}_{ri,j\pm 1/2,k}$ and $K^{n+1}_{ri,j,k\pm 1/2}$ are estimated by using the asymptotic weighting scheme proposed by Zaidel and Russo [1992]; and $k^{n+1}_{ri,j,k\pm 1/2}$ are calculated as the arithmetic mean of $K^{n+1}_{ri,j,k\pm 1}$ and $K^{n+1}_{ri,j,k}$, respectively. Ignoring the osmotic pressure head of the soil solution, Π , the sink term $S_w^{n+1}_{i,j,k}$ was approximated by $S_w^{n+1}_{i,j,k} = -R_{ei,j,k} K_{si,j,k} K^{n+1}_{ri,j,k} (\Psi_r^{n+1} - \psi^{n+1}_{i,j,k})$.

Finite-difference scheme (D1) has a truncation error of $O(\Delta t, \Delta x^2, \Delta y^2, \Delta z^2)$. It is convergent and unconditionally stable for the linear diffusion equation. The system of non-linear algebraic equations (D1) with respect to $\psi^{n+1}_{i,j,k}$ is solved by iterative means, applying the combination of Newton and Picard methods. Newton method of linearization is utilized for $\theta(\psi^{n+1}_{i,j,k})$ and $k^{n+1}_{ri,j,k\pm 1/2} = k_r(\psi^{n+1}_{i,j,k}, \psi^{n+1}_{i,j,k\pm 1})$, while the Picard method is used for the relative interblock conductivity corresponding to the capillary component of water flux. The resulting system of linear algebraic equations is solved by line successive overrelaxation (LSOR) method [e.g., Hageman and Young, 1981]

For each time-step, the CDE ((4.2)) governing solute transport in three-dimensions is approximated by an operator-splitting approach [e.g., Konikow and Bredehoeft, 1978; Wheeler and Dawson, 1987]. According to this approach, during the first stage of computation, only the advective part of equation is solved over the time interval Δt . During the second stage, this solution obtained at the first stage, becomes the initial condition for solving a pure dispersion equation over the same time interval Δt .

Numerical solution of the advection equation is obtained by a second-order accurate, explicit finite difference scheme proposed by Zaidel and Levi [1980]. This scheme is proven to describe accurately both smooth and steep concentration fronts without introducing notable artificial dispersion and spurious oscillations. This scheme involves three computational steps. During the first step, the values of solute concentrations at the interfaces between cells,

$c_{i\pm 1/2,j,k}^n$, $c_{i,j\pm 1/2,k}^n$ and $c_{i,j,k\pm 1/2}^n$ are estimated using an upstream quadratic interpolation and/or extrapolation procedure. For example, in case of positive flow direction along the x-axis interpolating parabola for face $i+1/2,j,k$ is based on concentration values $c_{i+1,j,k}^n$, $c_{i,j,k}^n$ and $c_{i-1,j,k}^n$ and extrapolating - on $c_{i,j,k}^n$, $c_{i-1,j,k}^n$ and $c_{i-2,j,k}^n$, respectively. Selection of interpolating or extrapolating parabola depends on the smoothness of solution in the vicinity of the interface. For uniform grid spacing:

$$c_{i+1/2,j,k}^n = \begin{cases} (3c_{i+1,j,k}^n + 6c_{i,j,k}^n - c_{i-1,j,k}^n)/8, & |\Delta_{1i}^n| \leq \max(|\Delta_{2i}^n|, |\Delta_{3i}^n|) \\ (15c_{i,j,k}^n - 10c_{i-1,j,k}^n + 3c_{i-2,j,k}^n)/8, & |\Delta_{1i}^n| > \max(|\Delta_{2i}^n|, |\Delta_{3i}^n|) \end{cases} \quad (D2)$$

where $\Delta_{1i}^n = c_{i+1,j,k}^n - c_{i,j,k}^n$; $\Delta_{2i}^n = c_{i,j,k}^n - c_{i-1,j,k}^n$; and $\Delta_{3i}^n = c_{i-1,j,k}^n - c_{i-2,j,k}^n$. To maintain numerical stability controlled by the standard Courant-Friedrichs-Lewy criterion and to obtain second-order temporal accuracy, the provisional values of $c_{i\pm 1/2,j,k}^{n+1/2}$, $c_{i,j\pm 1/2,k}^{n+1/2}$ and $c_{i,j,k\pm 1/2}^{n+1/2}$ at the intermediate time level $n+1/2$ are estimated during the second step (predictor) by approximating the advection equation at the interfaces $i\pm 1/2,j,k$, $i,j\pm 1/2,k$ and $i,j,k\pm 1/2$, respectively. During the third step (corrector), the trial concentration $c_{i,j,k}^*$ corresponding to the solution of advection equation is obtained from:

$$\begin{aligned} \frac{(\theta_{i,j,k}^{n+1} + \rho_b K_d) c_{i,j,k}^* - (\theta_{i,j,k}^n + \rho_b K_d) c_{i,j,k}^n}{\Delta t} = & - (q_{i+1/2,j,k} c_{i+1/2,j,k}^{n+1/2} \\ & - q_{i-1/2,j,k} c_{i-1/2,j,k}^{n+1/2}) / \Delta x_{i,j,k} - (q_{i,j+1/2,k} c_{i,j+1/2,k}^{n+1/2} \\ & - q_{i,j-1/2,k} c_{i,j-1/2,k}^{n+1/2}) / \Delta y_{i,j,k} \\ & - (q_{i,j,k+1/2} c_{i,j,k+1/2}^{n+1/2} - q_{i,j,k-1/2} c_{i,j,k-1/2}^{n+1/2}) / \Delta z_{i,j,k} \end{aligned} \quad (D3)$$

where $q_{i\pm 1/2,j,k}$, $q_{i,j\pm 1/2,k}$ and $q_{i,j,k\pm 1/2}$ are the cell-interface fluxes, calculated from the solution of (D1).

Note that if only upstream quadratic interpolation for concentration face values is used, the 3-D finite difference version of the well-known QUICK scheme [Leonard, 1979] is recovered from the described scheme for the advective component of solute transport. Combination of upstream interpolation and extrapolation can be viewed as a flux/slope limiting method [e.g., Sweby, 1984; Chakravarthy and Osher, 1985; Morton, 1996].

Dispersive fluxes are approximated by a standard central difference scheme at the second stage of solute transport simulations. The capability of the described scheme to solve the advection-dispersion equation for mesh Peclet number, Pe , varying from 2 to ∞ with mesh Courant number, Cr , varying from 0.1 to 1 was tested by using several 1-D and 2-D benchmark problems studied by Yeh [1990]. Results of these tests show that the numerical solutions obtained using the aforementioned procedure are in a very good agreement with the exact solutions for $Pe \leq 50$. Furthermore, there were no apparent oscillations exceeding $\pm 5\%$ of peak concentration in the solutions, even for $Pe = \infty$ (pure advection case). Numerical dispersion seems to be visible only for extremely large Peclet numbers. In this case accurate peak capturing and elimination of peak clipping problems can be achieved if more than 6-8 numerical cells are used in each direction per solute plume. The procedures outlined above completes a one time-step simulation of flow and transport.

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Fig. 4.14: Scaled standard deviation flux concentration, $[\langle C'(T;L)^2 \rangle]^{1/2} =$

$[\langle c_f'(T;L)^2 \rangle]^{1/2} / \int_0^\infty \langle c_f(T;L) \rangle dT$ crossing a control plane located at two different vertical distances, L (denoted by the numbers labeling the curves, in meters) from the injection zone, as a function of scaled travel time, $T = R_1(t)/L$. $R_1(t)$ is the longitudinal component of the coordinate location of the solute center of mass and t is time.

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(a)

F (1.1)

(b)

Scaled Velocity Covariance

Scaled Velocity Covariance

F 1.3

Scaled Displacement Covariance

F 1,4

Scaled Displacement Covariance

$F=1.5$

Asymptotic D'_{ij}

F 1,6

F 1.7

$$E_{11}(\xi)/E_{11}(0)$$

F 2.2.2

F 2.3

Normalized Velocity Covariance

F 2.4

F 2.6

F 3.1

F 3.2

F 3.3

$A(m^{-1})$

F 3.4

F 3.5

$$e = I_{wv} / I_{wh}$$

F 3.6

F 3.7

Amount of Water (m)

F 4.1

Soil Depth (m)

Water Saturation (m^3/m^3)

F 4.2

Soil Depth (m)

Pressure Head (m H_2O)

F 4.3

Soil Depth (m)

$\log K$

Soil Depth (m)

Head Gradient

F 4.5

Soil Depth (m)

F 4.6

F 4.7

F 4.8

Soil Depth (m)

Concentration (kg/m^3)

$F = 4.9$

Displacement (m)

$F = 4.10$

F 4.11

Effective Retardation Factor

Scaled Expected Flux Concentration

Scaled Standard Deviation of Flux Conc.

5 Estimation of Hydraulic Properties

5.1 Introduction and Previous Work

In the search for more accurate ways to predict the fate and transport of toxic substances in the environment, the need to understand the physical processes and soil characteristics affecting water movement cannot be overemphasized. Soil water provides a vehicle for transport of contaminants in solution, suspension or adsorbed to colloids, and can affect the movement of nonaqueous phase liquids through the soil matrix as well. Characterizing and accurately measuring soil hydraulic properties should be primary research goals for fate and transport modelers.

This topic has always been important to the agricultural community, which develops land management practices based on models of the physical processes involved in the entry of water into soil, the evaporation of water from the surface, and the subsurface flow of water to plant roots, drains and wells. However, in recent decades, growing concern over the global environmental crisis has provided a new use for vadose-zone solute transport modeling. Comprehensive conceptual models may prove to be of considerable importance to the prevention of groundwater contamination as well as to remediation efforts, but such models require very specific knowledge of the conductive and retentive properties of the soil matrix.

Characterizing Soil Hydraulic Properties

Since the derivation of the Richards equation (Richards, 1931), and subsequent rewriting as a nonlinear diffusion equation with a diffusivity parameter which is a function of water content (Childs and Collis-George, 1950), one of the greatest difficulties facing soil physicists has been to characterize the soil system accurately. Possibly the major limiting factor to progress in recent decades, as computers have become more powerful, and numerical solutions more available, has been the inadequate knowledge of the hydraulic properties required for accurate solutions of the governing transport equations (van Genuchten, 1980).

Quantifying these properties – the hydraulic conductivity, the water retention curve, and the diffusivity – has proven to be a daunting task. The accepted methods of measuring the hydraulic conductivity directly have proven inadequate to deal with the problems inherent in the Richards equation approach due to spatial and temporal variations in water content and matric potential in the field. If there were a reliable and rapid means for measuring hydraulic conductivity in the presence or absence of preferential flow, the research proposed herein would be superfluous. However, because measurement devices such as tensiometers are highly localized and have a finite response time, anomalies such as preferential flow are often missed by them, and any methodology (such as the instantaneous profile method or the air-entry permeameter) for measuring $K(\theta)$ that relies on such devices will not reveal the true hydraulic properties of the soil.

Neither do these methods necessarily agree with one another; for example, in one recent comparison study, the Guelph Permeameter in combination with the Gardner relationship for $K(\psi)$ gave results for unsaturated hydraulic conductivity three to four orders of magnitude less than predictions derived from the instantaneous profile method and a separate laboratory determination using undisturbed soil columns at a suction of -200 cm (Paige and Hillel, 1993). Simpler field methods, such as gravity drainage experiments, rely on water content changes

to measure the water flux, and are notoriously insensitive to preferential flow.

Even the measurement of the saturated hydraulic conductivity, which is merely one point on the $K(\theta)$ curve, has proven to be quite difficult. During a study conducted on soil with continuous macropores, it was concluded that it might be advantageous to define two saturated hydraulic conductivities: K_{sat} for the entire soil including macropores, and $K_{(sat)}$ for the matrix only, macropores subtracted (Bouma, 1982). In another comparison study, K_{sat} was measured by four different methods; the mean values determined by use of the rainfall simulator and the Guelph Infiltrimeter were two and a half to three times higher than those measured with the ring infiltrimeter and the Guelph Permeameter (Gupta et al., 1993).

Since actual field data regarding these properties are difficult, expensive and time-consuming to collect (Youngs, 1995), as well as of questionable accuracy, there have been many efforts to relate these parameters to physical characteristics of the soil matrix that can be measured with relative ease, such as particle size distribution or specific surface area. One of the earliest attempts along these lines was by Slichter in 1899; many other models followed, all based to some extent on Slichter's work: Terzaghi (1925), Kozeny (1927), Fair and Hatch (1933) and Carman (1938, 1939); these may be generalized as follows:

$$k = f(n)f(s)d^2 \quad (1)$$

where k is the permeability, d is a mean, or equivalent, grain diameter, $f(n)$ is a porosity factor and $f(s)$ is a shape factor related to the assumed geometrical shape of the pores and a tortuosity parameter (Bear, 1972). A major objection to this method is that such a model is not suited to a system with structure or aggregation, due to the fact that such structure affects the porosity and specific surface area to a negligible extent compared to the effect of aggregation on the permeability or conductivity. As was pointed out by Childs and Collis-George, these approaches work satisfactorily for saturated sands or certain industrial powders, but tend to fail when applied to other, less homogeneous systems (Childs and Collis-George, 1950).

Nevertheless the possibilities of using similar methods to predict soil hydraulic properties are still being explored. In 1981, Arya and Paris published their physicoempirical model to predict the water retention curve from particle-size distribution and bulk density (Arya and Paris, 1981). That was followed by the work of Haverkamp and Parlange in 1986, and a few years later, that of Alyamani and Sen; again, both of these models were based on grain-size distributions. Haverkamp and Parlange used shape similarity between the water retention curve and the cumulative particle-size distribution function to derive an expression for $h(\theta)$ which allows for hysteresis in the wetting and drying curves (Haverkamp and Parlange, 1986); they also pointed out the weakness in the Arya-Paris model, which is a non-unique definition of the pore-size/particle-size relationship. The Haverkamp-Parlange model was successful only for sandy soil with no organic matter content. The Alyamani-Sen model proposed to relate the hydraulic conductivity to the initial slope and intercept of the grain-size distribution curve (plotted on a log-log scale), and the difference between the mean particle diameter and a diameter termed the *effective* particle diameter (Alyamani and Sen, 1993). This analysis was done with aquifers in mind; the model was compared to data collected in sandy soil under saturated conditions. None of these studies have been able

to present evidence of a major improvement in particle-size models of hydraulic properties which is applicable to a wide range of natural soils.

Another popular modeling approach is based on pore-size distribution; these models tend to have a stronger theoretical basis for their assumptions, and fewer empirical coefficients. One of the earliest and best known was the model developed by E. C. Childs and N. Collis-George at the University of Cambridge (Childs and Collis-George, 1950). They derived the distribution function describing the pore space of a soil from the water retention curve with a graphical integration procedure, using simple statistical arguments to develop an estimation of the percentage of pores likely to be continuous, then established a link between the permeability and the pore-size distribution through the Hagen-Poiseuille equation. There were subsequent modifications of and extensions to this theory: Marshall, 1958; Millington and Quirk, 1961; Green and Corey, 1971; Mualem, 1976; van Genuchten, 1980, to mention a few of them; these have been used with varying degrees of success.

The Brooks and Corey model, (Brooks and Corey, 1964; 1966), also uses the pore-size distribution; this model was based on earlier work published in petroleum engineering literature dealing with flow systems containing two immiscible fluids (Burdine, 1953). Yet these approaches, although an improvement over the particle-size approach, have all experienced difficulties when applied to heterogeneous systems. All of them employ the water retention curve to some extent, yet research has shown that not only is there significant hysteresis between the sorption and desorption curves, but the desorption curve is not a unique function; rather there are a multitude of desorption curves possible, and which one will be measured in a given situation is highly dependent on the magnitude of the imposed drops in water content and the time to equilibrium after each step-change (Smiles et al., 1971).

Some researchers have avoided the pitfalls associated with attempting to derive expressions for $K(\psi)$ or $K(\theta)$ from basic physical principles by proposing equations for soil hydraulic properties which are entirely empirical in nature (Clapp and Hornberger, 1978). A list of some commonly used expressions for the hydraulic conductivity is given by Hillel, 1971:

$$\begin{aligned} K &= \frac{a}{\psi^m} \\ K &= \frac{a}{b + \psi^m} \\ K &= \frac{K_{sat}}{1 + (\psi/\psi_c)^m} \\ K &= a\theta^m \\ K &= K_{sat}W_s^m \end{aligned}$$

where K is the hydraulic conductivity; K_{sat} is the saturated hydraulic conductivity; a , b , and m are empirical constants to be determined for a particular data set by curve-fitting; ψ is the matric potential; ψ_c is the matric potential at $K = \frac{1}{2}K_{sat}$; θ is the volumetric water content and W_s is the relative degree of saturation. These expressions appear to work best for the data sets they were derived from; none of them has been employed with more than limited success in describing the hydraulic conductivity of field soil.

The aforementioned models range from those entirely based on the physics of flow through a porous medium to those which essentially are curve-fitting algorithms with empirical coef-

ficients. These deterministic approaches to the problem have repeatedly failed, except in the simplest, most homogeneous of systems; a user-friendly, accurate model which is applicable to a wide variety of soils remains an elusive goal.

Traditionally, hydrologists and soil scientists have attempted to apply macroscopic, deterministic laws derived in the laboratory to field scale formations, assuming homogeneity for simplicity's sake, with poor results (Dagan, 1986). Simplifying assumptions, such as gravity flow, designed to circumvent potential dilemmas like negative $K(h)$ values, or vertical homogeneity and piston flow, may lead to erroneous estimates of the true conductivity; effective or field-averaged properties may be meaningful only under certain very limited conditions (Bresler and Dagan, 1983). However, this risk of inaccuracy often has been deemed preferable to more exact approaches which may be prohibitive in terms of the time and labor involved (Libardi et al., 1980).

Preferential Flow

One consequence of spatial variability in field soils which has been the bane of deterministic modelers is preferential flow. Preferential flow occurs when water or other fluids bypass much of the soil matrix during an infiltration event, following the paths of least resistance through the soil and limiting the area through which the flux is actually passing. It has the potential to render chemical transport models nearly useless, due to the inability to predict or measure the high pore water velocities which reduce the chance for microbial degradation or adsorption to soil particles and expedite the arrival of dissolved chemicals in groundwater (Jury et al., 1986; Ghodrati and Jury, 1990). Briefly, some of the causes of preferential flow are: macropore structure (cracks, wormholes, etc.), significant lateral spatial variability in vertical hydraulic conductivity or other parameters (biotic or abiotic) (Elabd et al., 1986; Jury et al., 1986; van der Zee et al., 1990), fingered flow or unstable flow due to heterogeneous surface conditions (Hill and Parlange, 1972), water repellent soils (Bond, 1963), irrigation method or initial water content (Ghodrati and Jury, 1992; Flury et al., 1994), or funneling created by subsurface lenses or inclined planes of different texture than the surrounding matrix (Kung, 1990). Preferential flow in field soils has been called the rule rather than the exception (Flury et al., 1994). Clearly, lab and field studies using the same field soil might yield very different results for the hydraulic conductivity, because of the difficulties associated with retaining the original soil structure and boundary conditions in a lab setting.

In summary, the major problems associated with traditional methods of measuring and modeling the hydraulic properties of soil are:

- Direct measurement is expensive, time-consuming and sometimes severely limited by the capabilities and ranges of the instruments.
- The hydraulic properties of soil are complicated, non-linear functions which may demonstrate quite a lot of hysteresis between the wetting and drying curves.
- Spatial variability and preferential flow are ubiquitous in nature.
- Since available experimental data cannot completely describe the hydraulic properties in the water-content range of interest, it is necessary to extrapolate using one of the aforementioned models, which may be either empirical, quasi-empirical, or entirely theoretically based. However, none of the standard models has been shown to be accurate for real, spatially variable systems.

Statistical Transport Models

Recognizing the failure of the deterministic approaches, researchers have applied statistical theories to groundwater flow problems more and more frequently in an effort to deal with the spatial variability inherent in real field soils. This trend is well illustrated by Figure 3 from Dagan, 1986, which shows the cumulative number of articles on stochastic models of flow problems published by Water Resources Research as a function of time: the number begins near zero in 1977 and climbs to over one hundred by 1984. The basic approach when dealing with heterogeneity in this manner is to regard variables of interest such as the conductivity as a random space function characterized by the joint probability density function (pdf) of its numerical values at a certain number of points in space ($x_1, x_2, \dots, x_N$). Then the variable can be dealt with in terms of moments of the pdf, such as the expectation value or the covariance. The pdf for saturated hydraulic conductivity is generally distributed lognormally (Freeze, 1975). Stochastic methodology has been tested to predict dispersion in saturated conditions in aquifers, as it has the capability of predicting the time evolution of the variance (Freyberg, 1986; Garabedian et al., 1991). Clearly this approach requires large amounts of data for adequate characterization of the pdf.

Another means of applying stochastic theory assumes that the porous medium may be modeled as bundles of capillary tubes which do not exchange water or solute between them during transport; this is stochastic-convective stream tube modeling, which is part of transfer function theory as set forth in Jury and Roth, 1990. In this case, the probability density functions of interest are not spatial distributions of soil properties, but rather the solute travel time pdf, in the case of boundary value problems, or the travel distance pdf, for initial value problems (Jury and Scotter, 1994). These probability density functions, which are derived from solute breakthrough curves, are generally more easily measured than the spatial distribution of a particular hydraulic property.

In solute transport modeling, it is now clear from dye and tracer studies that the convection-dispersion equation often fails under field conditions (Steenhuis et al., 1990); Jury and Flühler (1992) showed that the CDE was only valid when the transverse mixing time in a volume of soil is short compared to the longitudinal travel time. Attempting to deal with this problem deterministically, by using the mobile-immobile water model for example, may become an exercise in curve-fitting, without representing the physical realities of the system in any meaningful way.

Transfer functions offer a different approach to transport modeling which has enjoyed some success; the issues of physical geometries and soil hydraulic properties are essentially ignored, and the soil is treated as a "black box", with solute transport predictions based on empirically determined breakthrough curves compared to the known input of a tracer (Jury and Roth, 1990). This method allows preferential flow to be dealt with to the extent that it can be characterized in the course of measuring the breakthrough curve, $C^f(z, t)$, from which the transfer function is derived. In 1994, departing from the "black box" approach, Scotter and Ross used the transfer function method to characterize the upper limit of solute dispersion due to convection; they derived $C^f(z, t)$ from the hydraulic conductivity for a worst-case scenario, which linked the transfer function of the system to its hydraulic properties.

Finally, a third statistically-based method uses scaling factors, derived from scaling theory based on the work of Miller and Miller, 1955, and extended by various researchers, to characterize the porous medium in terms of a scaling factor by which the hydraulic properties

are assumed to scale. The spatial distribution of the scaling factors must be determined for the field of interest; again, this approach seems demanding in terms of data requirements, since the spatial distribution of a soil property must be measured beforehand in order to use it. In order to be able to predict transport of water or solute in soil with this approach, the scaling factor pdf must be combined with a way to define the original reference function representing the conductivity or retention curve to be scaled. It is also necessary to confirm that the medium in question is actually a “Miller-similar” medium.

Scaling theory was introduced in 1955 by E. E. Miller and R. D. Miller in an effort to deal with some of the previously mentioned problems involved in describing the hydraulic conductivity (Miller and Miller, 1955, 1956). The fundamental idea behind this theory is that of a characteristic length scale or “magnifying factor” by which the geometry of one medium may be scaled to match the geometry of another medium; two such media are termed “similar”. The concept of similar media was extended and developed by several researchers, notably A. W. Warrick and D. R. Nielsen (Warrick et al., 1977, 1979; Warrick, 1993); the invariance of the Richards equation under scaling transformations was investigated by Sposito (Sposito and Jury, 1990) by means of Lie group analysis, which lead to the following conclusions: in the medium under study, the scaled diffusivity and conductivity must have either a power-law or exponential dependence on the relative saturation. In the original Miller and Miller paper, it was stated that, once again, this theory would be expected to do well for coarse-grained soil, but perhaps not so well for other types.

5.2 Measurement of $K(\theta)$ with a Travel Time Pdf

Following Scotter and Ross, we derived the pore water velocity from the unsaturated hydraulic conductivity- water content $K(\theta)$ function by making the following assumptions:

1. Gravity-driven water flow

$$J_w \approx K(\theta) \quad (2)$$

2. Stochastic-convective solute tracer flow
3. Steady state water flux J_w and water content Θ during leaching
4. Travel time and resident pdfs are defined through variable mass experiments

With these assumptions, we identify the hydraulic conductivity as an average flux made up of contributions from the pore-water velocities of different pore-size groups. The pore-water velocity of the group associated with a particular volumetric water content θ is

$$v(\theta) = \Delta\theta \xrightarrow{\lim} 0 \frac{\Delta K(\theta)}{\Delta\theta} = \frac{dK(\theta)}{d\theta} \quad (3)$$

Now we imagine that solute is added at a constant flux concentration C_B in a medium with hydraulic conductivity $K(\theta)$. By assumptions 1-4, the scaled flux concentration at $z = L$ and time $t = \tau$ is equal to the flow-weighted fraction of the wetted pore space that has travel times smaller than or equal to τ .

$$\frac{C^f(z, \tau)}{C_B} = \frac{\int_{\theta}^{\Theta} v(\theta') d\theta'}{\int_0^{\Theta} v(\theta') d\theta'} = \frac{\int_{K(\theta)}^{J_w} dK'}{\int_0^{J_w} dK'} = 1 - \frac{K[\theta(\tau)]}{J_w} \quad (4)$$

where $\theta(\tau)$ is the volumetric water content value at which the corresponding velocity from (3) is equal to z/τ , or equivalently that $\tau = z/v(\theta)$ is the travel time for solute to arrive at $z = L$.

Equations (3) and (4) provide a connection between the hydraulic properties and the solute transport observation. We may rewrite (3) as

$$\frac{d\theta}{dK} = \frac{1}{v(\theta)} = \frac{\tau}{z} \quad (5)$$

Equation (5) may be integrated after first changing variables from K to τ by using the derivative of (4)

$$\frac{dK}{d\tau} = -\frac{J_w}{C_I} \frac{dC^f(z, \tau)}{d\tau} = -J_w f^f(z, \tau) d\tau \quad (6)$$

Thus, (5) and (6) produce

$$\int d\theta' = \int \frac{\tau}{z} dK = -\frac{J_w}{z} \int \tau' f^f(z, \tau') d\tau' \quad (7)$$

Since θ must be zero when K is zero, we associate $\theta = 0$ with $\tau = \infty$. Thus, we may write

$$\theta = \frac{J_w}{z} \int_{\tau}^{\infty} \tau' f^f(z, \tau') d\tau' \quad (8)$$

whereas (4) may be rewritten as

$$K(\theta) = J_w \int_{\tau}^{\infty} f^f(z, \tau') d\tau' \quad (9)$$

Equations (8) and (9) define the $K(\theta)$ relationship implicitly.

Another form of this relation which is useful may be obtained by taking the Laplace transform of (8) and (9), with the result

$$\mathcal{L}\{\theta\} \equiv \hat{\theta} = \frac{\theta_m}{s} \left[1 + \frac{1}{\langle \tau \rangle} \frac{d\hat{f}}{ds} \right] \quad (10)$$

$$\mathcal{L}\{K\} \equiv \hat{K} = \frac{J_w}{s} [1 - \hat{f}] \quad (11)$$

where $\langle \tau \rangle = E[t]$, $\theta_m = J_w \langle \tau \rangle / z = \theta J_w$

A compact form for evaluating $K(\theta)$ may be obtained if $f^f(z, t)$ is lognormal

$$f^f(z, t) = \frac{1}{\sqrt{2\pi\sigma t}} \exp\left(-\frac{(\log(t) - \mu)^2}{2\sigma^2}\right) \quad (12)$$

Equations (8)-(12) may be combined, with the result

$$\theta(\tau) = \frac{J_w \langle \tau \rangle}{2z} \text{Erfc} \left[\frac{(\log(\tau) - \mu - \sigma^2)}{\sigma\sqrt{2}} \right] \quad (13)$$

$$K(\tau) = \frac{J_w}{2} \text{Erfc} \left[\frac{(\log(\tau) - \mu)}{\sigma\sqrt{2}} \right] \quad (14)$$

5.3 Examples of $K(\theta)$ functions for various pdfs

Figure 1 shows three lognormal travel time pdfs with different variance parameters σ and Figure 2 shows the corresponding $K(\theta)$ functions calculated with (13)-(14). As seen, increasing the variance creates a sharper drop in K at high water content. This is illustrated further in Figure 3, which shows the bimodal travel time

$$f(t) = \alpha f_1(t) + (1 - \alpha) f_2(t) \quad (15)$$

for three values of the parameter α . This pdf is intended to represent a soil with a preferential flow domain that has a rapid breakthrough described by $f_1(t)$. Figure 4 shows the corresponding $K(\theta)$ functions, illustrating the relation between preferential flow and the steepness of the conductivity curve near saturation.

5.4 Application to Existing Experimental Data

Field Study of Butters et al. (1989)

In 1989, Butters and colleagues monitored Br^- transport through the top 4.5 m of a 1.4 ha sandy loam. Solute was measured with solution samplers at 16 sites and each of the depths of 0.3, 0.6, 0.9, 1.2, 1.8, 3.0, and 4.5 m. From this information both local and field scale travel time pdfs were formed at each depth, which can be used to construct functions relating area-averaged water content to area-averaged hydraulic conductivity. Figure 5 shows a plot of the area-averaged 30 cm concentration from the Butters experiment, together with model fits from the convection dispersion model (CDE) and the convective-lognormal transfer function model (CLT) (see Eq. (12)) of Jury (1982).

The parameter fits of $\mu = 2.02, \sigma = 0.56$ to the CLT allow the field average $K(\theta)$ curve to be constructed from (13)-(14). This functional fit is shown in Figure 6. Also shown in Figure 6 is data for the field averaged function reported in Jury et al., (1990), obtained from air-entry permeameter measurements and the method of Russo and Bresler (1981). The curves are obviously very different. The air-entry values represent the mean of 56-different local measurements, subsequently fitted to an exponential model. The field average K is not the mean of the local values, so this method may have produced some error. There was substantial variation among the local permeameters, producing a high degree of uncertainty about the shape of the mean curve inferred from this method. Also, since the permeameter was drained by gravity flow, much of the lower range of the curve where the two functions seriously disagree was obtained by parameter extrapolation. This lower range is also the region where the stochastic-convective assumption is most likely to be violated.

The Butters et al., (1989) study was conducted at a daily flow rate of $J_w = 1 \text{ cm/d}$, which is the maximum K value that can be inferred from the solute outflow curve. Thus, the upper

range between this value and saturation cannot be estimated unless a solute experiment is conducted at the higher flow rates.

It is also possible to construct individual $K(\theta)$ functions from the local solute breakthrough curves recorded at individual sites, which gives an indication of the spatial variability of the function at a smaller scale. Figure 7 shows this for the 30 cm depth, along with a recreation of the area-averaged function. Note that the global K function is not the average of the local functions.

Lysimeter Study of Khan and Jury (1990)

Khan and Jury (1990) conducted solute transport experiments in disturbed and undisturbed large soil monoliths at three flow rates. The columns were drained by gravity, so that much of the lower part of the column was near saturation even when the upper part was not. This group of experiments was chosen to illustrate problems when the gravity flow hypothesis is violated. Figure 8 shows the fitted functions to the normalized outflow concentrations for the set of experiments performed in the 22 cm undisturbed column, and Figure 9 shows the corresponding calculated conductivity functions. Rather than tracing out the same curve at a somewhat lower water content, the curves are distinct. The reason for this is that the capillary fringe creates a matric potential gradient in the column which invalidates the gravity flow hypothesis. Thus, experiments that are not conducted at uniform water content cannot be used to calculate conductivity functions.

5.5 Materials and Methods

Solute Transport Experiments There were two soils used in this study: a coarse sand sieved from a 100-pound bag of 16 mesh commercial-grade silica sand, and a Tujunga loamy sand (mixed, thermic Typic Xeropsamments). The commercial sand was sieved twice, initially with a 1 mm sieve (discarding all particles larger than 1 mm) and then again with a 0.5 mm sieve (discarding all particles smaller than 0.5 mm) to obtain a sand with a narrow particle size distribution. The Tujunga soil was originally collected from a field site in Etiwanda, CA; it was passed through 1 mm sieve and mixed well prior to use.

The input solution consisted of deionized water with added reagent grade KBr, which was deaerated under vacuum for at least 24 hours prior to each experiment. The input concentrations varied somewhat from experiment to experiment; Table 1 lists several experimental parameters, including the values of C_0 and the measured saturated hydraulic conductivities for each solute transport run.

Experimental Apparatus Figure 10 shows the details of the system that was used to obtain the bromide breakthrough curves under saturated conditions. The apparatus consisted of a solute reservoir connected to a variable-speed pump, a glass soil column with a spout to allow overflow of excess water at the upper boundary in order to maintain a constant pressure head, and a rotating sample collector. The soil columns were 8.5 cm in diameter, and of variable length. Each column was attached with epoxy to a perforated base machined from polyethylene; prior to packing, two fine mesh stainless steel screens were inserted into the base to hold the soil in place. The packing depth in each column was the maximum height above the mesh screens to which a soil could be added while still keeping the soil surface below the overflow spout. The soil packing depths for the short, medium and long columns were 3.7, 6.25, and 29.0 cm, respectively. After packing, another mesh screen was placed on

the soil surface to allow the input solution to spread over the entire cross-sectional area of the column, rather than entering the matrix in a single, localized area directly beneath the input tube. The mesh also dispersed the force of the inflow, preventing disturbance of the soil surface.

Each column was saturated from below with deaerated, deionized water to expel as much air from the system as possible. After saturation, the coarse sand was ready for use; however, the Tujunga loamy sand contained enough organic matter to cause inaccuracies during the chemical analysis, and required the additional step of flushing the soil with water for periods of 2 to 4 hours before the output stream was clear enough to proceed with an experiment.

Sample sizes collected by the autosampler during the series of experiments varied between 3.0 mL and 35.0 mL, depending on the output flux from the column and the rotation speed of the sampler.

The system was designed to allow measurement of the saturated conductivity of the soil during each solute transport experiment, since K_{sat} can vary considerably between columns containing the same soil packed to the same bulk density. This may be seen in the coarse sand experiments, where K_{sat} was calculated at 0.45 cm sec^{-1} for the column used in Experiment 2, but was measured to be 0.20 cm sec^{-1} for Experiment 3; all of the sand columns were packed to the same bulk density of $1.44 \pm 0.02 \text{ g cm}^{-3}$.

Analytical Procedures Bromide samples were analyzed using an Alpkem RFA 300 Rapid Flow Analyzer, which is a segmented flow chemical analyzer designed to process samples at a high rate. The method of analysis used involved a modification of the standard phenol red method for bromide which allows for the speed of the analyzer. The standard method requires a twenty-minute wait between the addition of the last chemical reagent and colorimetric analysis, while the method developed at U.C. Riverside reduces the waiting period by an order of magnitude. (Sternberg 1997, Amer. Pub. Health Assoc. 1985).

Water Retention Procedures An experiment to measure the water retention curve of the coarse sand was performed using a plexiglass column with a diameter of 14.5 cm, mounted on a porous ceramic plate with an air entry value of 1 bar. The coarse sand described in the previous section was packed to a bulk density of 1.44 g cm^{-3} to form a layer 1.5 cm thick, for a total soil volume of 247.7 cm^3 .

The column was initially saturated, at which point a hanging water column was attached as shown in Figure 11. The experimental equipment was supported by a folding ladder. At the other end of the hanging water column was a calibrated glass vessel which collected the drainage water and allowed the volume to be measured accurately.

The free end of the hanging water column was then lowered to create negative matric potential, and the volume measurement was taken after the system came to equilibrium. The time intervals provided for the system to come to equilibrium ranged from 12 hours for the higher water contents to 24 hours for the drier end of the curve.

Direct Measurement of Unsaturated Hydraulic Conductivity

The column used in these experiments had a diameter of 14.8 cm, and was 10 cm high. During the sand experiments, two small TDR probes were inserted horizontally through the column wall and held in place with epoxy; the first was positioned two cm below the top of the column, and the second was 8.3 cm below the top of the column. The TDR probes allowed the water content at the top and bottom of the column to be compared during an experiment so that the boundary conditions could be adjusted immediately if the overall

water content was not uniform. For the experiments performed using the Tujunga loamy sand, another TDR probe was glued into the column approximately 5.5 cm below the top; this was done because the packing depth for the loamy sand was less than that of the coarse sand, due to the much lower permeability. Only the two lower probes were used during the Tujunga loamy sand experiments.

The TDR mini probes were triple-prong probes 10 cm in length; the rod diameters were ~ 0.75 mm and were positioned ~ 0.7 cm apart. The data collection system consisted of a Tektronix 1502B Metallic TDR Cable Tester in conjunction with a Campbell Scientific CR10 Measurement and Control Module and CR10KD Keyboard Display.

The entire column was mounted on a large vacuum chamber (Soil Measurement Systems) attached to a vacuum regulator. This provided the primary means of adjusting the water content in the lower part of the column. The soil preparation and packing procedures were the same as described in previous sections.

Deionized water entered the sand via a sprinkler head which had the same diameter as the column. A random vibration source (in the form of a vibrating toy) was attached to the support that held the the sprinkler head to create small random motions in the horizontal direction; this allowed the the water to be distributed more evenly over the surface.

5.6 Coarse Sand Experiments

The packing depth of the sand in the initially saturated columns was 9.0 cm; it was packed to the same bulk density used in the bromide transport experiments: $\rho_b \sim 1.44$ g cm⁻³. The sand was saturated with deaerated, deionized water and attached to the vacuum chamber; the experiment began with the highest possible water flux (just below ponding), and the weakest possible vacuum in the chamber. The input water flux to the top of the column and amount of vacuum at the lower boundary were varied until the TDR water content readings were within $\sim 2\%$ of each other and had remained stable for several minutes.

When the system reached equilibrium, the input flux and vacuum were simultaneously disconnected from the column, to keep the water content from changing. The volume flux was measured and converted to hydraulic conductivity, and the entire column was weighed to determine the mass of water contained in the sand, so that the fractional water content could be calculated.

Subsequently, the column was reattached to the vacuum chamber, the input water flux rate was lowered, and the vacuum raised, until a new equilibrium point was attained, whereupon the measurements described above were repeated.

For the initially dry column experiment, the sand in the column was initially water-free; we began with a very low input water flux and a fairly high vacuum at the lower boundary. Once again, the flux rate and vacuum were adjusted until the TDR readings were close enough to each other and had remained the same for some time, suggesting that the water content was uniform and had reached equilibrium.

The measurements of flux and water content were done as described above, then the column was reattached to the vacuum chamber and the flux rate was raised, while the vacuum was reduced, until the system reached a new equilibrium at a higher water content.

Tujunga Loamy Sand Experiments

The initially saturated column was packed with Tujunga loamy sand to a depth of 5.5 cm

and a bulk density of 1.5 g cm^{-3} , and was saturated with deaerated, deionized water before being attached to the vacuum chamber; again, the experiment began with the highest possible water flux, and the least possible vacuum in the chamber. The boundary conditions were varied in the manner described in the previous section for the coarse sand until equilibrium was reached, when the flux and water content were measured. The entire process was then repeated at a lower flux rate and higher vacuum, resulting in a new equilibrium at a lower water content.

This experiment, beginning with saturated conditions, was performed twice with the Tujunga loamy sand; the results are presented in Figure XY.

Just as described in the above section for the coarse sand, an experiment was done using dry Tujunga loamy sand. The beginning flux rate was quite low and the vacuum at the lower boundary needed to be fairly high to keep a water table from forming at the bottom of the column. The protocol for this experiment duplicates that of the experiment performed with the coarse sand under initially dry conditions. The results are plotted with those of the initially saturated experiments in Figure XY.

Coarse Sand Experiments Figure 12 presents the results from two of the transport experiments which were performed using the coarse sand, in which the outflow from a step function input was measured. Figure 13 shows the corresponding pdf obtained by numerically differentiating the cdf curve from figure 12.

Tujunga Loamy Sand Experiments Figure 14 shows the cumulative outflow curve obtained for the Tujunga loamy sand in two of the experimental runs, and 15 shows the corresponding pdf obtained by numerically differentiating the cdf curves. Note that the average breakthrough time is nearly a factor of 10 longer for the loamy sand than the coarse sand. Note also the suggestion of some bimodality in the outflow curve for this soil.

5.7 PDF Model Predictions

Figure 16 shows the cdf from one of the coarse sand experiments fitted by the lognormal cumulative distribution function:

$$P(\mu, \sigma, t) = (1/2)\text{Erfc}[(\mu - \log t)/(\sqrt{2}\sigma)] \quad (16)$$

and figure 17 presents the corresponding $K(\theta)$ curves calculated for the coarse sand using (13)-(14). Examples of a fit to breakthrough data and subsequent model prediction for the hydraulic conductivity function for Tujunga loamy sand are shown in Figures 18 and 19. These latter cdfs are fitted by the weighted sum of two lognormal cumulative distribution functions, due to the bimodal nature of the breakthrough data:

$$P(t : \mu_1, \sigma_1, \mu_2, \sigma_2) = \frac{1}{2}(\alpha\text{Erfc}[(\mu_1 - \log t)/(\sqrt{2}\sigma_1)] + (1 - \alpha)\text{Erfc}[(\mu_2 - \log t)/(\sqrt{2}\sigma_2)]) \quad (17)$$

Figure 20 compares the model hydraulic conductivity functions for the two soils used in this study, showing that the hydraulic regimes are completely different.

5.8 Water Retention Measurement

Figure 21 shows the results of the water retention study for the coarse sand. The moisture release curve is extremely sharp, corresponding to a soil that loses most of its water with a

modest suction.

Mualem-van Genuchten Model Predictions for Coarse Sand The van Genuchten equation (van Genuchten 1980)

$$\frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{[1 + \alpha(-h)^N]^{-M}} \quad (18)$$

for describing the water retention function $h(\theta)$ was fitted to the experimental data. The $K(\theta)$ curve was plotted from the output produced by RETC, a FORTRAN 77 program (van Genuchten, Leij & Yates 1991) produced at the U.S. Salinity Laboratory in Riverside, CA, which allows various models to be used to predict hydraulic functions for unsaturated soils. The model chosen for the plots shown below (Figure 22) was the Mualem model for predicting the relative hydraulic conductivity (Mualem 1976).

5.9 Comparisons of the Two Models

In order to compare the two models, the model predictions are plotted together in Figure 23 for all the sand experiments.

Another way to compare the models is to back-calculate what the pdf and cdf would look like for this model-generated $K(\theta)$ curve, if the data had been produced by a solute transport experiment, rather than a water retention measurement. Using the model first presented by Scotter and Ross (1994), which postulates that the hydraulic conductivity function may be used to predict solute transport data, assuming stochastic-convective flow, the cdf and pdf for the Mualem-van Genuchten model fit were plotted, and are presented in Figure 24 with the actual breakthrough data for the coarse sand.

5.10 Comparison With Direct Measurement

Figure 25 and Figure 26 show the direct measurement results for the coarse sand and Tujunga soil, respectively obtained under initially wet and initially dry conditions. When the soil is initially wet, there is a region in which the direct and solute transport-generated curves agree reasonably well, and below which the model assumptions break down. The Van Genuchten-Mualem curves are shown for comparison.

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Table 1: System variables for the bromide transport experiments.

Expt. No.	Soil	Soil Packing Depth (cm)	Input C_o (Br^- , mg L^{-1})	Ponded head (cm)	K_{sat} cm sec^{-1} (sand) cm min^{-1} (Tujunga)
1	sand	6.25	362.5	1.1	0.37
2	sand	6.25	365.1	0.5	0.45
3	sand	29.0	465.5	1.0	0.20
4	sand †	29.0	348.7	0.7	0.42
5	Tujunga †	3.7	476.7	0.1	0.10
6	Tujunga †	3.7	369.8	0.05	0.19
7	Tujunga ¶	6.25	488.1	0.1	0.07
8	Tujunga ¶	6.25	365.5	0.1	0.06

† low-level Br^- contamination in H_2O used to saturate column

‡ flushed soil 2 hrs to remove organics

¶ flushed soil 4 hrs to remove organics

Figure 1: Lognormal travel time pdfs for three different values of the log variance S

Figure 2: Calculated $K(\theta)$ curves corresponding to the travel time pdfs in Figure 1, assuming that $\Theta = 0.5$ and $K(\Theta) = 100$.

Figure 3: Hypothetical bimodal travel time pdfs

Figure 4: Calculated $K(\theta)$ curves corresponding to the bimodal travel time pdfs in Figure 3

Figure 5: Field data averaged over 16 sampler sites, together with model fits for the experiment of Butters et al., (1989)

Figure 6: Field-average $K(\theta)$ function for the 0-30 cm depth constructed from the data of Fig. 5 using (13)-(14).

Figure 7: Local $K(\theta)$ functions for the 0-30 cm depth constructed from the local solute outflow curves recorded at individual sampling sites using (13)-(14).

Figure 8: Concentration outflow curves at three flow rates from the experiment of Khan and Jury (1990).

Figure 9: Local $K(\theta)$ functions calculated from the curves of Figure 8.

Figure 10: Schematic of Experimental Design for Solute Transport Studies

Figure 11: Schematic of Experimental Design for Water Retention Curve Measurement

Figure 12: Plots of normalized cumulative concentration versus time (coarse sand in medium length column).

Figure 13: Plots of probability density functions (coarse sand in medium length column).

Figure 14: Plots of normalized cumulative concentration versus time (Tujunga soil in short column).

Figure 15: Plots of probability density functions (Tujunga soil in short column).

Figure 16: The cdfs from the medium column-coarse sand experiments fitted by the lognormal cumulative distribution function.

Figure 17: Plots of PDF model predictions for $K(\theta)$ for coarse sand in medium column

Figure 18: The cdfs from the short column-Tujung soil experiments fitted by the dual lognormal cumulative distribution function.

Figure 19: Plots of PDF model predictions for $K(\theta)$ for Tujunga loamy sand in short column

Figure 20: Comparison of PDF model predictions for $K(\theta)$ (cm min⁻¹) for coarse sand and Tujunga loamy sand in medium column

Figure 21: Plots of water retention data for the coarse sand

Figure 22: Plots of water retention data fit and corresponding Mualem-van Genuchten model prediction of $K(\theta)$ for the coarse sand

Figure 23: Plots of PDF model prediction and Mualem-van Genuchten model prediction of $K(\theta)$ for the coarse sand in medium and long columns.

Figure 24: Plots of the cdf and pdf generated from the Mualem-van Genuchten model prediction of $K(\theta)$ for the coarse sand, compared to actual data from the medium column runs.

Figure 25: Plots of the predicted hydraulic conductivity function for the coarse sand from the solute transport experiments and from direct measurement in initially wet- and initially-dry soil.

Figure 26: Plots of the predicted hydraulic conductivity function for the Tujunga soil from the solute transport experiments and from direct measurement in initially wet- and initially-dry soil.

6 Evaluation of the Research Achievement

We were able to meet all of our goals in this BARD project, as articulated in the project proposal objectives. In this section, we discuss the significance of our results relative to the original expectations

6.1 Objective 1

A major effort was put forth in Israel to develop a stochastic analysis of a macroscopically heterogeneous medium using the technique of stochastic continuum analysis. This approach, which is well developed in ground water research, faces serious obstacles in its extension to the nonlinear regime of unsaturated flow. Despite these limitations, Israeli investigators have developed the analysis rigorously for an important class of problems involving flow of reactive and nonreactive chemicals under steady unsaturated flow. The field-scale velocity covariance tensor, the foundation stone of macrodispersion analysis, has been derived from local soil properties and their variability, producing a large-scale description of the medium that embodies all of the local variability in a statistical sense. Special cases of anisotropic medium properties not aligned along the flow direction and of spatially variable solute sorption were analysed in detail, revealing a dependence of solute spreading on subtle features of the variability of the medium, such as cross-correlations between sorption and conductivity.

US Investigators spent considerable effort developing and testing a novel method for measuring hydraulic conductivity at the scale of observation through the interpretation of a solute transport outflow curve as a stochastic-convective process. This undertaking provided a host of new $K(\theta)$ relationships for existing solute experiments and also laid the foundation for future work developing a self-consistent description of flow and transport under these conditions. Numerical codes were developed for calculating $K(\theta)$ functions for a variety of solute pulse outflow shapes, including lognormal, Fickian, Mobile-Immobile water, and bimodal. Testing of this new approach against conventional methodology was mixed, and agreed most closely when the assumptions of the new method were met. We conclude that this procedure offers a valuable alternative to conventional methods of measuring $K(\theta)$, particularly when the application of the method is at a scale (e.g. an agricultural field) that is large compared to the common scale at which conventional $K(\theta)$ devices operate. Israeli investigators approached the same problem from a numerical perspective, by studying the feasibility of inverting a solute outflow signal to yield the hydraulic parameters of the medium that housed the experiment. We found that the inverse problem was solvable under certain conditions, depending on the amount of noise in the signal and the degree of heterogeneity in the medium. Thus, our joint analysis of the problem produced both an approximate and exact solution to the problem of estimating hydraulic conductivity from solute outflow, as well as conditions under which a given approach was to be used.

6.2 Objective 2

Israeli investigators constructed a realistic three dimensional model of transient water and solute movement in a heterogeneous medium that contains plant roots. The approach taken was to generate a single realization of this complex flow event, and examine the results to see

whether features were present that might be overlooked in less sophisticated model efforts. One such feature revealed is transverse dispersion, which is a critically important component in the development of macrodispersion in the longitudinal direction. The lateral mixing that was observed greatly exceeded that predicted from simpler approaches, suggesting that at least part of the important physics of the mixing process is embedded in the complexity of three dimensional flow. Another important finding was the observation that variability can produce a pseudo-kinetic behavior for solute adsorption, even when the local models used are equilibrium. This numerical experiment has clearly illustrated that small-scale phenomena can have macroscopic consequences.

6.3 Objective 3

Research on this objective was conducted at both institutions. Israeli investigators concentrated on analysing the utility of the stochastic continuum approach under different conditions (reactive or inert solutes, anisotropy, root system, transient and steady flow), while US investigators addressed the problem of how complex a local model is required to obtain useful information in a regional simulation of pesticide and nitrate contamination of ground water. The options for local representation in stochastic modeling focused on three aspects: water flow (quasisteady versus transient), dispersion (convective-dispersive versus stochastic-convective), and rate-process (equilibrium versus kinetic) representations. In each case, options for the representation were compared relative to performance and data requirements.

7 Description of the Cooperation

Although the main emphasis of the Israel group was numerical modeling and that of the US group physical experimentation, the two institutes conducted their research from a design scheme that produced different perspectives on common problems. Field scale water and solute processes are of sufficient complexity that current methods are often found lacking in representing flow and transport under natural conditions. Our research was designed to create new tools for addressing the problems created by heterogeneous media, for which we designed both an experimental and theoretical attack. Wherever possible, Israeli and US investigators used complementary approaches to the same problem to maximize the effectiveness of the investigation. In one case, the same problem, calculating hydraulic properties from observation of solute outflow, was studied from two different perspectives. In the US, emphasis was placed on creation of a macroscopic field scale discharge versus water storage function from the outflow, whereas in Israel it was the construction of the covariance structure of the local K field. In each case, the goal was to develop a large scale description of the hydraulic properties from a solute transport experiment conducted at the same scale.

The US investigators worked primarily with travel time pdfs as the foundation for solute transport. To provide an additional means of comparison, Israeli investigators generated travel time pdfs in their numerical experiments to allow a basis for comparison between the two approaches.

8 Publications

The following publications were generated from the BARD project reported herein.

1. O'linger Joann, 1997. Measurement of unsaturated hydraulic conductivity with a solute transport experiment. PhD Thesis, University of California, Riverside.
2. O'linger J., W. Pichler, and W. Jury, 199x. Measurement of unsaturated hydraulic conductivity with a solute transport experiment. (in preparation)
3. Russo, D., 1995a. On the velocity covariance and transport modeling in heterogeneous anisotropic porous formations I. Saturated flow. *Water Resour. Res.*, 31: 129-137.
4. Russo, D., 1995b. On the velocity covariance and transport modeling in heterogeneous anisotropic porous formations II. Unsaturated flow. *Water Resour. Res.*, 31: 139-145.
5. Russo, D., 1995c. Stochastic analysis of the velocity covariance and the displacement covariance tensors in partially saturated heterogeneous anisotropic porous formations. *Water Resour. Res.*, 31: 1647-1658.
6. Russo, D., 1997. A note on the velocity covariance and transport modeling in partially saturated heterogeneous porous formations of two- and three-dimensional structures, *Adv. Water Resour.* (in press).
7. Russo, D., J. Zaidel, and A. Laufer, 1994a. Stochastic analysis of solute transport in partially-saturated heterogeneous soil: I. Numerical experiments, *Water Resour. Res.*, 30, 769-779.
8. Russo, D., J. Zaidel, and A. Laufer, 1994b. Stochastic analysis of solute transport in partially-saturated heterogeneous soil: II. Prediction of solute spreading and breakthrough, *Water Resour. Res.*, 30, 781-790.
9. Tseng, P. W. Jury, and M. Flury, 1997. Stochastic Solute Transport Modeling of Regional Non-point Source Pollution. AGU/ SSSA Special Publication from 1997 Chapman Conference, Riverside, CA October, 1997.

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