Numerical evaluation of solute dispersion and dilution in unsaturated heterogeneous media

Olaf A. Cirpka
Universität Stuttgart, Institut für Wasserbau, Stuttgart, Germany

Peter K. Kitanidis
Stanford University, Department of Civil and Environmental Engineering, Stanford, California, USA

Received 19 February 2002; revised 19 March 2002; accepted 19 March 2002; published 6 November 2002.

[1] We investigate flow and solute transport in a heterogeneous unsaturated soil under gravity-driven flow conditions using a direct simulation Monte Carlo method. We account for the cross correlation between the heterogeneous fields of unsaturated flow parameters representing a silty loam. We determine through particle tracking the statistical moments of the travel time distribution for nonpoint injection of a conservative tracer. The one-particle mean and variance characterize the mean arrival time and spreading of solute integrated over an entire horizontal cross section of the domain, whereas the two-particle semivariogram characterizes the spreading observed at individual points. From these quantities we derive macrodispersivities and effective dispersivities. The latter reflect solute dilution. Owing to the nonlinearity of unsaturated flow the dispersivity values at a given depth vary with the mean infiltration rate. The two-particle semivariogram hardly differs from the one-particle variance of travel time at low infiltration rates, whereas dilution and macrodispersion rates differ significantly at high infiltration rates. We compare the dispersivities determined through particle tracking with approximations from linear stochastic theories based on the covariance of the Eulerian velocity field [Dagan, 1988; Fiori and Dagan, 2000]. These linear stochastic theories slightly underestimate both dispersivity types. We present parametric models for the two types of dispersivities as function of the infiltration rate and the depth.

INDEX TERMS: 1875 Hydrology: Unsaturated zone; 1832 Hydrology: Groundwater transport; 1869 Hydrology: Stochastic processes; KEYWORDS: unsaturated zone, heterogeneous media, solute dispersion, dilution, two-particle moments


1. Introduction

[2] Solute dispersion and dilution are important processes in the transport of agrochemicals and other nonpoint-source pollutants in unsaturated soils. By solute dispersion we describe the predominantly vertical spreading of the solutes due to the spatially variable velocity field. Using macrodispersive parameters in a one-dimensional macroscopic model, we can approximate the vertical profile of concentrations averaged over a large horizontal cross section. This is of interest, for example, in the estimation of the mass flux of contaminants into groundwater by recharge. The determination of macroscopic parameters enables us to infer spreading of a pulse introduced at the surface as it travels through the unsaturated zone toward the water table. The macrodispersive description, however, does not reflect the temporal spreading and maximum concentration measured at a single observation point. Simulated and measured concentration profiles in two- and three-dimensional heterogeneous soils [Tseng and Jury, 1994; Russo et al., 1998; Ursino et al., 2001a, 2001b] show that the local concentration maxima are significantly higher than the maximum values of the cross-sectional average. This is due to concentration fluctuations which have been studied intensively in saturated-zone transport [Kapoor and Gelhar, 1994; Andrićević, 1998; Fiori and Dagan, 2000; Vanderborght, 2001]. Most of these studies have focussed on the concentration variance, that is, the variability about the mean concentration. Expected concentration maxima, however, may more directly be evaluated from quantities related to solute dilution such as the dilution index [Kitanidis, 1994], the effective dispersion coefficient for a point-like injection [Dentz et al., 2000], or the apparent dispersivity of mixing [Cirpka and Kitanidis, 2000a]. Experimental studies on solute dilution in the unsaturated zone are scarce. Ursino et al. [2001a] were the first to determine the dilution index from experiments in an unsaturated sandbox.

[3] The effects of heterogeneity on solute transport in the unsaturated zone have been studied intensively through experiments [see, e.g., Ellsworth and Jury, 1991; Forrer et al., 1999; Ursino et al., 2001b], numerical studies [see, e.g., Tseng and Jury, 1994; Roth and Hammel, 1996; Harter and Yeh, 1996; Birkholzer and Tsang, 1997; Russo et al.,...
1998], and theoretical analysis [Russo, 1993; Russo et al., 1994; Hammel and Roth, 1998; Vanderborght et al., 1998; Harter and Zhang, 1999; Sun and Zhang, 2000]. Owing to the nonlinearity of the governing equations, the flow patterns depend on the mean infiltration rates. In particular, it has been shown for Miller-similar media [Miller and Miller, 1956] that preferential flow paths are in fine-texture regions at low infiltration rates and in coarse-texture regions at high ones [Roth, 1995]. At intermediate infiltration rates, the heterogeneous medium may become almost homogeneous leading to minimal dispersivity values [Roth and Hammel, 1996; Birkholzer and Tsang, 1997; Hammel and Roth, 1998]. As pointed out by Hammel and Roth [1998], such a minimum in the dispersivity value occurs only when the fluctuations in the matrix potential are strongly correlated with those of the effective conductivity. In the case of Miller-similar media, the relationship between these fluctuations is deterministic. While the Miller-similarity is convenient for numerical studies, the assessment of unsaturated flow parameters from various experimental studies by Carsel and Parrish [1988] shows that the van Genuchten parameters \( \alpha \) and \( N \), the residual water contents \( \theta_r \), and the saturated hydraulic conductivity \( K_s \) are characterized best as cross-correlated fields. In the present study, we will use such cross-correlated fields which is an extension to the numerical studies cited above.

In the upscaling of unsaturated flow and transport through numerical studies, a particular problem is that under general conditions, the matrix-potential, saturation, and velocity fields are nonstationary even if the medium properties are stationary [Zhang and Winter, 1998; Sun and Zhang, 2000]. With the exception of gravity-driven flow, stationary fields of soil properties result in nonstationary fields of the matrix potential. Another source of nonstationarity in the matrix potential is the application of boundary conditions such as a fixed potential at the outflow boundary. This type of boundary condition was used, e.g., by Roth [1995] and Birkholzer and Tsang [1997]. Additional deviations between analytical and numerical results may result from constant-flux boundary conditions, including no-flux conditions at the vertical faces as applied in all numerical studies cited above. In saturated flow studies, it is common to exclude stripes near the boundaries in the evaluation of macrodispersion [Chin and Wang, 1992]. In three-dimensional models, this procedure is highly inefficient because it means discarding results from significant parts of the domain. These issues are worth considering when one compares numerical results based on volume averaging with analytical results based on ensemble averaging.

An expedient approximation of a stationary field over a finite domain is through a periodic one. Both stationary and periodic fields can be statistically characterized by their autocovariance and cross-covariance functions. Although both describe an infinite domain, only the periodic field can be completely represented through a single unit cell, which has finite dimensions. In fact, a stationary field can be viewed as a periodic one at the limit of a unit cell with infinite dimensions. Dykaar and Kitanidis [1992] used spatially periodic fields to determine the effective saturated conductivity of heterogeneous media. By applying periodic boundary conditions, the hydraulic head fluctuations along a boundary of the unit cell are identical to those at the opposite boundary, and a streamline leaving the domain at a certain face re-enters the domain at the opposite face. Using no-flux and fixed-head boundary conditions imposes restrictions which, e.g., tend to underestimate the effective conductivity or flow velocity when results from the whole domain are used; when results near the boundaries are discarded, the sampling uncertainty is increased. Using periodic boundary conditions for the fluctuations, the results from the whole domain can be used in the analysis of effective conductivity, macrodispersion, and effective dispersion. Artifacts in the evaluation of dispersion due to the periodicity can be minimized by choosing a unit cell that is large enough for a particle to “forget” its initial location by local-scale dispersion while being advected once through the unit cell [Kitanidis, 1992]. A specific advantage of periodic media is that the generation of fields and the analysis of the simulated results can be done in the spectral domain using discrete Fourier-transform techniques. Thus, in the present study, we will use a periodic representation of soil heterogeneities. We will restrict our analysis to gravity-driven flow thereby ensuring that the matrix-potential, saturation, and velocity fields are also periodic.

The main objective of the present study is to derive parameters describing solute dispersion and dilution in unsaturated soils as function of the depth and the mean infiltration rate. We derive the mean and variance of one- and two-particle travel time statistics. With these parameterized expressions, we may determine linear transfer functions describing solute transport in the unsaturated zone. By distinguishing between one- and two-particle travel time statistics we derive measures applicable to the cross-sectionally averaged concentration and the expected point concentration at a certain depth.

### 2. Governing Equations

For the description of flow in variably saturated porous media, we use the widely accepted Richards’ equation:

\[
\frac{\partial S(\psi_m)}{\partial \psi} \frac{\partial \psi}{\partial t} - \nabla \cdot (K(\psi_m) \nabla \psi) = - \frac{\partial K(\psi_m)}{\partial \psi} \tag{1}
\]

where

\[
\psi_m = \min(\psi, 0) \tag{2}
\]

in which \( S(\psi_m) \) (dimensionless) is the water saturation and \( \theta_s \) (dimensionless) is the volumetric water content at full saturation, i.e., the effective porosity. \( K(\psi_m) \) [m/s] is the unsaturated hydraulic conductivity, \( \psi_m \) [m] is the matrix potential, \( z \) [m] the depth, that is, the vertical spatial coordinate pointing downwards, and \( \psi \) [m] is either, at negative values, the matrix potential or, at positive values, the pressure head. At steady state, equation (1) simplifies to:

\[
\nabla \cdot (K(\psi_m) \nabla \psi) = \frac{\partial K(\psi_m)}{\partial \psi} \tag{3}
\]
The specific discharge \( q \) [m/s] and the seepage velocity \( v \) [m/s] are given by:

\[
q = -K(\psi_m)(\nabla \psi - \mathbf{e}_z) \tag{4}
\]

\[
v = \frac{q}{S(\psi_m)\theta_z} \tag{5}
\]

where \( \mathbf{e}_z \) (dimensionless) is the unit vector pointing downward. The contribution \( K(\psi_m)\mathbf{e}_z \) to the specific discharge vector \( q \) is due to gravity. Note that the components \( q_y \) and \( v_z \) are positive in downward direction. For the constitutional relationships \( K(\psi_m) \) and \( S(\psi_m) \) on the local scale we use the Mualem-van Genuchten parameterization [van Genuchten, 1980]:

\[
K(\psi_m) = K_s \sqrt{S(\psi_m)} \left(1 - \left(1 - S(\psi_m)\frac{\theta_z}{\theta_s}\right)^n\right)^{\frac{1}{n-1}} \tag{6}
\]

\[
S(\psi_m) = S_r + (1 - S_r)S_r(\psi_m) \tag{7}
\]

\[
S_r(\psi_m) = \left((-\alpha\psi_m)^\theta + 1\right)^\frac{1}{\theta} \tag{8}
\]

in which \( K_s \) [m/s] is the saturated hydraulic conductivity, \( N \) (dimensionless) and \( \alpha \) [1/m] are the van Genuchten parameters, \( S_r \) (dimensionless) is the residual water saturation, and \( S_r(\psi) \) (dimensionless) is the effective saturation.

[8] We consider \( K_s, N, \alpha, \) and \( S_r \) as spatially cross-correlated parameter fields, whereas \( \theta_z \) is assumed constant. Then, the spatial correlations of the matrix potential \( \psi_m \) and the seepage velocity \( v \) depend on the spatial correlation of the unsaturated flow parameters and the boundary conditions. We restrict our analysis to gravity-dominated unsaturated flow at steady state. Under these conditions, the mean gradient of \( \psi_m \) is zero. We also consider spatial periodicity, that is, the distributions of the independent parameters repeat themselves exactly at distances \( L_x, L_y, \) and \( L_z \) [m] in the three spatial coordinates, e.g.,

\[
K_i(x,y,z) = K_s(x + iL_x, y + jL_y, z + kL_z) \tag{9}
\]

for all integer numbers \( i, j, k \) and similar equations for \( N, \alpha, \) and \( S_r \) rather than \( K_s \). Consequently, the dependent variables \( \psi_m, S, q, v \) are also periodic. As already stated, the periodic representation of the soil properties is a finite representation of stationary fields.

[9] Taking volume averages, denoted by bars, we determine the upscaled relationships, \( S(\psi_m), q_x(\psi_m), v_x(\psi_m), \) and \( C_{\psi \psi}, h(\psi_m) [\text{m}^2/\text{s}^2] \) which is the autocovariance function of the vertical seepage-velocity component with the separation vector \( h \) [m]. Because in gravity-driven flow the mean gradient of the total potential is \(-e_z\), the mean vertical specific discharge \( q_z(\psi_m) \) is identical to the upscaled vertical conductivity \( K_{zz}^* \). The functional relationship between the volume-averaged quantities, e.g. \( S(\psi_m) \), differs from the functional relationship for the corresponding local quantities, \( S(\psi_m) \). As an example, the van Genuchten parameterization for the water-saturation, \( S(\psi_m) \), yields a value of one for a matrix potential \( \psi_m \) of zero. However, in a heterogeneous field with an average matrix potential \( \psi_m \) of zero, spatial variability leads to local values of \( \psi_m \) smaller than zero. Hence, the average saturation \( S \) is also smaller than one. Consequently, the principal directions of the autocovariance functions of the soil parameters to be the horizontal and vertical directions. Under these conditions, the entries \( K_{xx}^* \) and \( K_{yy}^* \) are negligible. If either the local conductivity tensor or the covariance function of the soil properties is not oriented in the horizontal and vertical directions, \( K_{xx}^* \) and \( K_{yy}^* \) become significant (see, e.g., the experimental study of Ursino et al. [2001b] in which a sandbox model was filled with tilted lenses). The numerical procedure presented in this study could easily be extended to include these type of structures.

[10] Based on the seepage velocity distribution, we investigate solute transport governed by the well-known advection-diffusion equation:

\[
\frac{\partial c}{\partial t} + v \cdot \nabla c - D \nabla^2 c = 0 \tag{10}
\]

in which we have considered that at steady state the specific-discharge field is free of divergence. In equation (10), \( c [\text{kg/m}^3] \) is the flux concentration, that is, the solute flux in the vertical direction divided by the vertical component of the specific discharge vector. Using this definition of the flux concentration requires that there is a downward component of the specific discharge at each point within the domain, which is satisfied for gravity-driven flow. \( D [\text{m}^2/\text{s}] \) is the effective diffusion coefficient considered uniform. In the numerical implementation of the present study, we will neglect local dispersion in the vertical direction. It is well known that longitudinal local dispersion can essentially be added to the macro- and effective dispersion coefficients derived without it [Fiori, 1996]. It is therefore not necessary to include it explicitly in the upsampling procedure. By contrast, transverse local dispersion, leading to an exchange between streamtubes, has been identified as the major factor in the transfer of longitudinal spreading to mixing [Kapoor and Gelhar, 1994; Pannone and Kitanidis, 1999; Cirpka and Kitanidis, 2000a]. Therefore we cannot neglect it if we want to study solute dilution. We assume that molecular diffusion is the only mechanism contributing to local horizontal dispersion, which is a legitimate assumption for unsaturated flows. Typical values of local transverse dispersivities and seepage velocities are on the order of \( 10^{-4} \) m and \( 10^{-3} \) m/s, respectively, leading to a velocity-proportional contribution to transverse dispersion of \( 10^{-1} \) m/s that is significantly smaller than the molecular diffusion coefficient on the order of \( 10^{-9} \) m/s.

[11] At the initial time \( t_0 \) [s], we introduce a solute pulse at the top of the soil column into the domain. No further solute mass is in the domain. The injected solute flux density \( \dot{m}_w(t_0, x, y) \) at a point \((x, y)\) on the surface \(z = 0\), is assumed proportional to the infiltration rate:

\[
\dot{m}_w(t_0, x, y) = \dot{c}(t_0) q_z(x, y, 0) = c_0 q_z(x, y, 0) \tag{11}
\]
in which $c_0$ [kg/m$^2$] is the mean injected solute mass per area. This initial condition is identical to assuming a uniform distribution of the flux concentration $c$ at the top of the soil column:

$$c(t_0, x) = c_0 \delta(z)$$

(12)

From the periodicity of the flow field and the uniform horizontal distribution of the initial concentration follows horizontal periodicity of the concentration at all times:

$$c(x + L_x, y, z, t) = c(x, y + L_y, z, t) = c(x, y, z, t)$$

(13)

In the vertical direction, the concentration distribution is not periodic, and thus transport must be considered over the semi-infinite soil column. At the top, the mass flux is zero after the initial injection. At the limit of infinite depth, the flux concentration and all its derivatives tend to zero. In solving the transport problem, note that the solute exiting at the bottom of a unit cell enters the underlying unit cell which has an identical flow field.

### 3. One-and Two-Particle Travel Time Statistics

[13] In the present study, we analyze solute transport in a Lagrangian framework. Consider a Dirac-pulse injection into the solute flux at the surface with a mass density $c_0$ [kg/m$^2$] at time zero as defined by equation (11). The distribution of the injected solute flux at the initial state may be expressed as particle distribution with a density proportional to that of the vertical specific-discharge component [Vanderborght et al., 1998]. From the tracking of a sufficiently large number of particles, we estimate the distribution of the particle travel time $\tau(z)$ [s] at depth $z$ [m]. Then, the flux-weighted average of the concentration $\bar{c}(z)$ over the entire horizontal cross section at depth $z$ is related to the probability density function (pdf) of travel times $p(\tau, z)$ [1/s] by [Shapiro and Cvetkovic, 1988]:

$$\bar{c}(\tau, z) = \frac{c_0}{q_0} p(\tau, z)$$

(14)

in which the hat denotes the flux-weighted cross-sectional average. The one-particle travel time distribution $p(\tau, z)$ is characterized by the mean $\mu_\tau(z)$ [s] and variance $\sigma_\tau^2(z)$ [s$^2$] of travel time at depth $z$:

$$\mu_\tau(z) = E[\tau(z)]$$

(15)

$$\sigma_\tau^2(z) = E[(\tau(z) - E[\tau(z)])^2]$$

(16)

in which $E[]$ denotes expected values that can be replaced by cross-sectional averages at the limit of an infinite cross-sectional area. From the definition of flux-weighted concentration in equation (14), it is obvious that the mean $\mu_\tau(z)$ and variance $\sigma_\tau^2(z)$ of the one-particle travel time distribution are identical to the first and second central temporal moments of the flux-weighted concentration $\bar{c}(\tau, z)$ normalized by its zeroth moment. Therefore we may define the mean seepage velocity $\bar{v}_z$ and the macrodispersivity $\alpha_\tau(z)$ by the vertical gradients of the one-particle moments $\partial \mu_\tau/\partial z$ and $\partial \sigma_\tau^2/\partial z$ [Cirpka and Kitanidis, 2000a]:

$$\bar{v}_z = \left( \frac{\partial \mu_\tau}{\partial z} \right)^{-1}$$

(17)

$$\alpha_\tau(z) = \frac{\sigma_\tau^2}{2} \frac{\partial \sigma_\tau^2}{\partial z} - D \bar{v}_z$$

(18)

[14] In the stochastic analysis of temporal moments by Shapiro and Cvetkovic [1988], the mean $\mu_\tau(z)$ and variance $\sigma_\tau^2(z)$ were related to the spatial statistics of the inverse Eulerian velocity $v^{-1}$ [s/m]. According to Cvetkovic et al. [1992], the harmonic mean of the Eulerian velocity will be observed by particles at small distances, whereas the arithmetic mean is appropriate at large ones. Vanderborght et al. [1998], however, showed that the arithmetic mean is appropriate at all travel distances when a uniform flux concentration rather than a uniform resident concentration is assumed at the initial state. The latter study also includes a comparison of several approximations of $\sigma_\tau^2(z)$, the easiest of which implies that the variance of travel time $\sigma_\tau^2(z)$ at distance $z$ is the variance of longitudinal one-particle displacement $\sigma_X(z)$ at the corresponding mean travel time divided by $\bar{v}_z$ [Rubin and Dagan, 1992]. Applying the latter identity, linear stochastic theory for strictly advective transport in stationary media yields the following expected macrodispersivity [Rubin and Dagan, 1992]:

$$\alpha_\tau(z) = \frac{\gamma'}{\bar{v}_z} \int_0^z C_{\tau, \tau}(0, 0, \zeta) d\zeta$$

(19)

in which $\gamma' = K_p/K*$ is the ratio of the geometric mean of the spatially variable conductivity and the effective macroscopic conductivity in the direction of flow. The correction factor $\gamma'$ is justified by the observation that the stochastic-analytical results for macrodispersivities in three-dimensional domains based on the variability of the log conductivity are more accurate when the first-order approximation $K_p$ rather than the second-order approximation $K_p/(1 + \sigma_\tau^2 K_p/6)$ is used as macroscopic conductivity [Chin and Wang, 1992].

[15] Including local dispersion, which in this study is restricted to effective diffusion, does not change the estimate of $\mu_\tau(z)$, whereas it does alter $\sigma_\tau^2(z)$ in two ways. Longitudinal diffusion adds a term of $2 z D \bar{v}_z^2$ to $\sigma_\tau^2(z)$ which can easily be separated from transport without longitudinal diffusion. By contrast, transverse diffusion makes the velocity distribution experienced by the particles more uniform, leading to decreased values of $\sigma_\tau^2(z)$. Linear stochastic theory gives closed-form expressions for macrodispersion affected by local transverse diffusion. By assuming that the $\partial \sigma_\tau^2/\partial z$ at depth $z$ is proportional to the time-dependent macrodispersion coefficient at time $z \bar{v}_z$, we get the macrodispersivity at a certain travel distance from Dagan’s [1998] expression:

$$\alpha_\tau(z) = \frac{\gamma'}{\bar{v}_z (2 \pi / st_D)^{d/2}} \int_0^\infty \frac{\exp \left( \frac{-z^2 \gamma_s}{\bar{v}_z^2} \right)}{is \gamma_s - s^2 D} S_{\tau, \tau}(s) ds$$

(20)

in which $d$ is the dimensionality of the domain, $s$ is the vector of wave numbers with $\gamma_s$ corresponding to the $z$-
direction, \( s^2 = s \cdot s \), and \( S_{\nu z}(s) \) is the power spectral density function of the vertical seepage velocity, which is the Fourier transform of the corresponding covariance \( C_{\nu z}(h) \):

\[
S_{\nu z}(s) = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} C_{\nu z}(h) \exp(ih \cdot s) dh
\]  

[16] One-particle moments are useful in the analysis of the flux-weighted cross-sectionally averaged concentration \( \bar{c} \). The temporal moments characterize the mean and spread of the breakthrough curve of \( \bar{c} \) at a given depth \( z \). The corresponding maximum concentration can be estimated by parameterizing this breakthrough curve, e.g., by the lognormal or the inverse Gaussian distribution. However, the averaging operation produces a smooth and spread out breakthrough curve. At single points within the domain, we will observe more peaked breakthrough curves with a mean travel time fluctuating around \( \mu_t \). We refer to breakthrough curves at single points as local ones. We may characterize the local breakthrough curves at all points at depth \( z \) by their temporal moments, and subsequently take the flux-weighted cross-sectional average of the moments. While the average of the first moment at a given depth \( z \) is identical to the first moment of the average concentration \( \mu_t(z) \), the average of the locally determined second central moment is considerably smaller than the second central moment of the averaged concentration. In fact, the difference between the two quantities is the variance \( \sigma_t^2(z) \) of the locally determined first moment [Kitanidis, 1988; Cirpka and Kitanidis, 2000a].

[17] We may analyze the problem of locally measured breakthrough curves by considering the corresponding adjoint problem. So far, we have assumed an injection into the flux spread out over the entire surface of the soil column, and we wanted to analyze the flux-weighted average of the second central moment of breakthrough curves measured at single points at depth \( z \). In the adjoint problem, we inject the solute into the flux at a single point, take the flux-weighted average of the concentration at depth \( z \), and analyze its second central temporal moment. We repeat this for all possible injection points. weight the corresponding second central moments with the infiltration rate at the injection point, and take the average over all injection points. Since the velocity field is stationary, the resulting temporal moments of breakthrough curves are identical for both problems. The corresponding spatial moments for a point-like injection have been studied in the context of effective dispersion by Dentz et al. [2000] and, using a different terminology, Vanderborght [2001].

[18] In the Lagrangian framework, we approximate the second central temporal moment originating from a point injection by the semivariogram of two-particle travel time \( \gamma_{tt} \):

\[
\gamma_{tt}(z) = \frac{1}{2} E[(\tau_1(z) - \tau_2(z))^2]
\]  

in which \( \tau_1(z) \) and \( \tau_2(z) \) are the times that two particles, introduced at the same surface location, need to reach depth \( z \). We estimate the expected value in equation (22) by a flux-weighted cross-sectional average of the injection location. That is, we introduce many particle pairs, each starting at a different horizontal position, determine half the squared difference in travel time to reach the depth \( z \) and take the flux-weighted average over all particle pairs. Obviously, if there were no local dispersion, the travel times \( \tau_1(z) \) and \( \tau_2(z) \) of the two particles starting at the same location would be identical, and \( \gamma_{tt}(z) \) would be zero. The travel paths, and therefore the travel times, of particles starting at the same location differ only due to the random displacement caused by diffusion.

[19] In analogy to the one-particle moments, we define an effective dispersivity \( \alpha_x[m] \) from the two-particle semivariogram of arrival time \( \gamma_{tt}(z) \) and the mean seepage velocity by [Cirpka and Kitanidis, 2000a]:

\[
\alpha_x = \frac{\nu^2}{2} \frac{\partial \gamma_{tt}}{\partial z} - \frac{D}{\nu_t}
\]  

\( \alpha_x \) is a measure of solute dilution. Dentz et al. [2000] and Fiori and Dagan [2000] derived closed-form expressions for the time-dependent effective dispersion coefficient by linear stochastic theory in an Eulerian and Langrangian framework, respectively (see also the derivation by Vanderborght [2001]). In analogy to the macrodispersivity, we can approximate the depth-dependent effective dispersivity \( \alpha_z(z) \) from these closed-form expressions by taking the value at time \( z/\nu_t \):

\[
\alpha_z(z) = \alpha_z(z) - \frac{1}{\nu_t(2\pi)^{3/2}} \int_{-\infty}^{\infty} \frac{ix_2 \nu_t + s^2 D}{s^2 \nu_t^2 + s^2 D^2} \exp\left(-\left(\frac{ix_2 \nu_t + s^2 D}{\nu_t}\right)\right)
\]

\[
\alpha_z(z) = \alpha_z(z) - \frac{1}{\nu_t(2\pi)^{3/2}} \int_{-\infty}^{\infty} \frac{ix_2 \nu_t + s^2 D}{s^2 \nu_t^2 + s^2 D^2} \exp\left(-\left(\frac{ix_2 \nu_t + s^2 D}{\nu_t}\right)\right) S_{vz}(s) ds
\]

[20] An additional quantity of two-particle travel time statistics is the two-particle covariance of travel time \( \sigma_{tt} \):

\[
\sigma_{tt} = E[(\tau_1(z) - E[\tau_1(z)])(\tau_2(z) - E[\tau_2(z)])] = \sigma_t^2 - \gamma_{tt}
\]

While \( \sigma_t^2 \) is a measure of the temporal spread of the cross-sectionally averaged concentration and \( \gamma_{tt} \) of the concentration at a point, \( \sigma_{tt} \) describes the uncertainty in predicting the mean travel time at a point at depth \( z \). Cirpka and Kitanidis [2000b] conceptualized a heterogeneous medium by parallel advective-dispersive streamtubes, each with a different uniform velocity, in which the dispersivity within all streamtubes is given by the travel path averaged effective dispersivity, and the weights of the streamtubes are derived from the pdf of mean arrival times. The latter may be approximated by \( \mu_t(z), \sigma_{tt}(z) \) and a parametric model.

4. Methods

4.1. Generation of Cross-Correlated Fields

[21] We consider a representation of a heterogeneous silt loam with cross-correlated parameters \( K(x), S(x), \alpha(x), \) and \( N(x) \). For the generation of the parameter fields, we
assume that the Johnson transformations of the parameters, given by Carsel and Parrish [1988] for the chosen soil texture, are normally distributed. The back-transformation to the original physical variables is given by:

\[
K_x = \min(\max(K_x), A_{K_x}) \frac{B_{K_x}}{26} \quad (26)
\]

\[
S_x = \frac{\exp(S_x)B_{S_x} + A_s}{1 + \exp(S_x)} \quad (27)
\]

\[
\alpha = \min(\max(\exp(\alpha), A_\alpha), B_{\alpha}) \quad (28)
\]

\[
N = \frac{B_N\exp(N) + A_N}{1 + \exp(N)} \quad (29)
\]

in which the tilde denotes the transformed parameters. The statistical parameters and the transformation parameters \(A_i\) and \(B_i\) are listed in Table 6 of Carsel and Parrish [1988].

We assume that the autocorrelation parameters of all generated quantities are identical and that the cross-correlation is fully determined by the correlation between different quantities at zero separation. We generate four independent autocorrelated fields with zero mean, unit variance, horizontal integral scale \(L_h\) of 0.5 m and vertical integral scale \(L_v\) of 0.1 m at a grid of 5 m \(\times\) 10 m \(\times\) 4 m with 64 \(\times\) 128 \(\times\) 256 cells using the spectral approach of Dykaar and Kitanidis [1992] which is identical to that described by Roth [1995]. We use the Gaussian autocovariance model:

\[
C(h) = \exp\left(-\frac{\pi}{4} \left(\frac{h_x^2 + h_y^2}{L_x^2} + \frac{h_z^2}{L_z^2}\right)\right) \quad (30)
\]

From the independent fields \(\tilde{p}(x)\), we generate cross-correlated fields \(\tilde{p}^*(x)\) by multiplication with the Cholesky-decomposition \(R\) of the cross-covariance matrix \(C_{pp}(0)\) of the transformed variables at zero separation:

\[
\tilde{p}^*(x) = \tilde{p}(x)R \quad (31)
\]

with

\[
R^T R = C_{pp}(0) \quad (32)
\]

The values of the \(R\) entries are given in Table 7 of Carsel and Parrish [1988]. The fields \(\tilde{p}^*(x)\) have zero mean, and the correct autocovariance and cross-covariance matrices. The transformed variables \(K_x(x), S_x(x), \alpha(x)\), and \(N(x)\) are determined by adding the corresponding mean. The transformed parameters are finally back-transformed to physical variables using the equations given above.

4.2. Simulation of Unsaturated Flow

We solve Richards’ equation at steady state, equation (3), for prescribed mean potentials \(\psi\) using a cell-centered Finite Volume Method with Picard iteration for linearization. The effective hydraulic conductivity at each interface is the harmonic average of the adjacent control volumes corresponding to the matrix potentials at the previous iteration. At the first iteration, we assume a uniform distribution of \(\psi\). Periodicity of the fluxes is implemented by connecting control volumes at opposite sides of the unit cell. The resulting system of equations is symmetric and singular, that is, there is an infinite number of solutions differing by an unknown constant because no value of \(\psi\) has yet been specified. We obtain a valid solution using a conjugate gradient solver with algebraic multigrid preconditioning [Ruge and Stüben, 1987] and subsequently adjust the \(\psi\)-field such that the mean potential \(\bar{\psi}\) equals the prescribed value. The nonlinearity of the system is particularly strong when saturated and unsaturated regions alternate, that is, at \(\psi \approx 0\). In these cases, we might get strong fluctuations in the \(\psi\)-field from iteration to iteration. We stabilize the method by relaxation: the effective hydraulic conductivity for the next iteration is a weighted average of the value used in the last iteration and the value corresponding to the value of the matrix potential in the latest iteration.

We evaluate the distributions and volume averages of the potential \(\psi\), the saturation \(s\), the specific discharge \(q\), and the seepage velocity \(v\). The effective hydraulic conductivity \(K_z(\bar{\psi})[m/s]\) equals \(q_z\). Due to spatial periodicity, we can determine the power-spectral density function \(S_{vz}(s)\) and the autocovariance function \(C_{vz}(h)[m^2/s^2]\) of the vertical seepage velocity \(v_z\) using the discrete Fourier transformation:

\[
S_{vz}(s) = \mathcal{F}(v_z)\text{conj}(\mathcal{F}(v_z)) \quad (33)
\]

\[
C_{vz}(h) = \mathcal{F}^{-1}(S_{vz}(s)) \quad (34)
\]

in which \(\mathcal{F}\) and \(\mathcal{F}^{-1}\) denote the discrete Fourier transformation and its inverse, respectively. \(v_z\) is the fluctuation of \(v_z\) about its mean, and “conj” denotes the complex conjugate. The multiplication in equation (33) is performed independently for each value of \(s\). Due to the periodicity of the velocity field, the values of the autocovariance function \(C_{vz}\) are identical at separations \(h\) and \((0, 0, L_z) - h\). By substituting \(C_{vz}\) into equation (19), we evaluate the depth-dependent macrodispersivity \(\alpha_d(z)\) expected for advective transport from first-order theory. By substituting \(S_{vz}\) into equations (20) and (24), we retrieve the expected macrodispersivity \(\alpha_d(z)\) and effective dispersivity \(\alpha_e(z)\) accounting for local diffusion.

4.3. Simulation of Transport

We simulate advective transport by particle tracking using the semi-analytical approach of Pollack [1988]. Horizontal diffusion is simulated by a standard random-walk approach. The particles are advected from each horizontal plane to the underlying one. Subsequently, the horizontal displacement is randomly generated from a normal distribution with a mean of zero and a standard deviation of \(\sqrt{2D \Delta t}\) in both horizontal directions, where \(D\) is set to the typical value of \(10^{-9} m^2/s\) and \(\Delta t\) is the time needed in the vertical displacement step. Vertical diffusion is neglected in the simulations thus guaranteeing that each particle passes each observation plane exactly once. Periodicity is achieved by reintroducing a particle, which is leaving the unit cell via a boundary, at the opposite boundary of the unit cell. For each particle we track the position within the unit cell and in which cell the particle is located.
In our calculations, the injected mass-flux at the surface is proportional to the infiltration rate. In a 2-D particle tracking study, Vanderborght et al. [1998] achieved this type of boundary condition by placing the particles with a density proportional to the vertical specific discharge component \( q_z \). In 3-D, this approach is less straight-forward. Rather than placing the particles, or particle-pairs, in a nonuniform fashion, we use a uniform particle distribution and weight the results (travel time, \( \tau(z) \)), squared travel time, \( \tau^2(z) \), and travel time difference squared, \( (\tau_1(z) - \tau_2(z))^2 \) with the relative infiltration rate \( q_1/q_2 \) at the starting point.

Since the velocity field is periodic and does not exhibit any trend, we can introduce the particles at any depth level and consider the vertical displacement rather than the absolute vertical coordinate. By introducing particle pairs at the centers of all horizontal interfaces between control volumes, we arrive therefore at a true volume average of \( \tau(z) \), \( \tau^2(z) \), and \( (\tau_1(z) - \tau_2(z))^2 \). The flux-weighted values of \( \mu_r(z) \), \( \sigma^2_r(z) \), and \( \gamma_{\tau r}(z) \) are then evaluated by:

\[
\mu_r(z) = \frac{\sum_i q_i(x_i) (\tau(x_i, z) + \tau(z, x_i))}{q_z/2} \quad (35)
\]

\[
\sigma^2_r(z) = \frac{\sum_i q_i(x_i) (\tau(x_i, z) + \tau(z, x_i))^2}{2 q_z} - \mu_r^2(z) + 2 \mu_r(z) D z^2 / \sigma^2 \quad (36)
\]

\[
\gamma_{\tau r}(z) = \frac{\sum_i q_i(x_i) (\tau(x_i, z) - \tau(z, x_i))^2}{2 q_z} + 2 \mu_r(z) D z^2 / \sigma^2 \quad (37)
\]

where \( x_i \) denotes the starting point of particle pair \( i \), and \( z \) is the vertical displacement. The term \( 2 \mu_r(z) D z^2 / \sigma^2 \) in the evaluation of \( \sigma^2_r(z) \) and \( \gamma_{\tau r}(z) \) originates from vertical diffusion that has been neglected in the particle-tracking method.

5. Results

5.1. Flow Calculation

The first two rows of Figure 1 show the generated distributions of hydraulic properties. Most obvious is the almost perfect correlation of log(\( K_s \)) and log(\( \alpha \)) with a correlation coefficient of 0.986 [Carsel and Parrish, 1988]. The van Genuchten parameter \( N \) is also correlated to log(\( K_s \)) and log(\( \alpha \)), but to a much lesser extent. As an example, the resulting distributions of \( \psi, S, K(\psi_m), \) and \( q_z \) at a mean potential \( \psi = -0.30 \) m are shown in the third and fourth row of Figure 1. While the distributions of the saturation \( S \) and the unsaturated conductivity \( K(\psi_m) \) directly reflect the anisotropic soil structure, the vertical discharge component \( q_z \) shows vertical correlation at a larger scale than the other parameters. The variability of both the saturation \( S \) and the potential \( \psi \) indicates that neither upscaled approaches based on a uniform saturation as that of Russo [1993] nor those based on a uniform matrix potential as that of Hammel and Roth [1998] reflect the true variability of unsaturated flow fields.

5.2. Dispersivities Expected from Linear Theory

We calculate the autocovariance function \( C_{v\psi}(h) \) and spectral density function \( S_{v\psi}(s) \) of the vertical seepage velocity \( \psi \) and approximate the macrodispersivity \( \alpha_\psi(z) \) and effective dispersivity \( \alpha_\psi(z) \) expected from first-order theory by substitution of \( C_{v\psi}(h) \) and \( S_{v\psi}(s) \) into equations (19), (20), and (24). Figure 5 shows the expected dependence of \( \alpha_\psi \) on the travel depth \( z \) and the mean infiltration rate \( q_m \) for strictly advective transport. The dependence on the travel distance \( z \) is sinusoidal; \( \alpha_\psi \) increases strongly at

\[
K^{*}_s(\psi) = K^{*} \sqrt{S_e} \left( 1 - \left( 1 - S_e^{\psi} \right)^{\alpha \psi} \right)^2 \quad (38)
\]

\[
S(\psi) = S_e + (1 - S_e) S_e \quad (39)
\]

\[
S_e(\psi) = \left( (-\alpha \min(\psi - \psi_m, 0))^{\psi} + 1 \right)^{-\alpha \psi} \quad (40)
\]

where \( \psi_0 \) is the positive potential at which the system turns from partially unsaturated to water-saturated. This additional parameter is necessary since the potential-fluctuations may lead to locally unsaturated conditions at slightly positive values of \( \psi \). The macroscopic saturated conductivity \( K^{*}_s \) of \( 2.35 \times 10^{-7} \) m/s is determined from saturated flow calculations. The other parameters, evaluated by minimizing the mean squared errors of \( K^{*}_s(\psi) \) and \( S(\psi) \), are listed in Table 1. The curves reflecting the fitted parameters are included in Figures 2 and 3. Note that the values of the macroscopic parameters differ considerably from the values where the peaks of the distributions of the local parameters are located which are \( K_s = 3.11 \times 10^{-7} \) m/s, \( S_e = 0.17 \), \( N = 1.38 \), and \( \alpha = 1.65/m \) [Carsel and Parrish, 1988].
Figure 1. Distribution of unsaturated flow parameters in the unit cell (rows 1 and 2) and results of the unsaturated flow calculation at a mean potential \( \psi \) of \(-0.30\) m (rows 3 and 4). See color version of this figure at back of this issue.
small \( z \) values; at \( z \approx L_z/2 \), the increase is minimal because of the smaller spatial correlation of \( v_z \) at these separations, whereas \( \partial \alpha / \partial z \) gets larger when \( z \) approaches \( L_z \) because of the periodicity of \( C_{v_zv_z}(h) \). The latter increase would not occur if the velocity field were stationary rather than periodic. A second important tendency of \( \alpha^* \) is the non-monotonic dependence on the mean infiltration rate \( q_z \). At rates of a few millimeters per year the expected macrodispersivity is minimal. The same qualitative behavior has been found and explained by Roth and Hammel [1996], Birkholzer and Tsang [1997], and Hammel and Roth [1998], although for different parameters leading to a minimum of \( \alpha^* \) at higher infiltration rates. The strong correlation of the van Genuchten parameter \( \alpha \) and the saturated conductivity \( K_s \) causes preferential flow in the coarse-texture regions at high infiltration rates and in the fine-texture regions at low ones.

It may be noted that the impact of the correction factor \( \gamma \) in equation 19 is quite high at high infiltration rates. At full saturation, \( \gamma \) increases the expected dispersivities by more than thirty per cent. As pointed out by Chin and Wang [1992], \( \gamma \) can be viewed as a quasi higher-order correction. The latter authors showed that macrodispersivities at \( \sigma_{K*}^2 \) values of 2.25 can be approximated quite well by linear stochastic theory when the first-order rather than the second-order approximation of effective conductivity is used.

As mentioned above, the approximation of \( \alpha_z(z) \) by equation (19) does not include effects of local dispersion on macrodispersion. These effects are accounted for in equation (20). The corresponding expected macrodispersivity \( \alpha \) is shown in Figure 6 as function of the travel depth \( z \) and the mean infiltration rate \( q_z \). At high infiltration rates, the two graphs are almost indistinguishable. At low infiltration rates, however, the expected macrodispersivities when accounting for diffusion are much lower than those if transport is restricted to advection alone. Particularly, the values of \( \alpha_z \) do not increase with decreasing infiltration rates at very low \( q_z \) values. At very low infiltration rates,
horizontal diffusion makes a particle sample all velocities while being advected once through the unit cell. By contrast, the characteristic time of advection is too small at high infiltration rates for diffusion to have a significant effect on one-particle travel time statistics.

[34] The effective dispersivity expected from linear theory, equation (24), is shown in Figure 7 as function of the travel depth \( z \) and the mean infiltration rate \( \bar{q} \). At very low infiltration rates, the two types of dispersivities reach practically identical values. This is consistent with the observation that \( \alpha^* \) does not increase at very low infiltration rates although the velocity field is more heterogeneous. At the very low infiltration rates, the characteristic times of advection and transverse diffusion are at least at the same order. At higher infiltration rates, however, transverse diffusion is much slower than longitudinal spreading due to nonuniform advection, and the expected effective dispersivity values \( \alpha_e \) differ significantly from the expected macrodispersivity values \( \alpha^*(z) \).

[35] For infiltration rates \( \bar{q} \) higher than one tenth of \( K^*_s \), the expected values of \( \alpha_e \) become almost independent with increasing infiltration rates. This can be explained by two counteracting effects at higher infiltration rates. The mean advective travel time is inversely proportional to \( \bar{q} \), so that transverse diffusion has less time to develop at higher infiltration rates. Conversely, the variability in the velocity fields increases with higher infiltration rates. At long distances, the effective dispersivity \( \alpha_e \) approaches the value of
macrodispersivity $\alpha_\ast$. That is, the higher $\alpha_\ast$, the stronger is the driving force for $\alpha_\ast$. In the present application, these two effects cancel each other out when $\bar{q}_z$ is approximately larger than 740 mm/year.

5.3. Numerical Travel Time Statistics

[36] The one-particle travel time statistics characterizes the behavior of the flux concentration averaged over the entire horizontal cross section. To begin with, we want to test whether the first and second central moments can directly be approximated from the Eulerian velocity field. In a strictly macroscopic description, the seepage velocity is approximated by the mean specific discharge $\bar{q}_z$, the porosity $q_s$, and the mean saturation $S$:

$$v_\bar{z} \approx \frac{\bar{q}_z}{\theta, S} \quad (41)$$

This expression holds only when $q_z$ and $S^{-1}$ are uncorrelated. We compare the resulting velocity with the mean seepage velocity evaluated from the mean arrival time $\mu_\tau$ by equation (17) which corresponds to the mean particle velocity. Results not shown indicate that the prediction of the mean arrival time $\mu_\tau$ using the macroscopic flow parameters $\bar{q}_z$, $S$, and $\theta$ is quite accurate with errors less than 2% in the entire range of travel distances and infiltration rates considered. This indicates, that the arithmetic mean of the Eulerian seepage velocity is indeed the expected value of the particle velocity if the input is a uniform flux concentration [Vanderborght et al., 1998]. Also, the correlations of $q_z$ and $S^{-1}$ are rather small.

[37] Figure 8 shows the macrodispersivity $\alpha_\ast$ as evaluated from the one-particle moments by equation (18) as function of the travel depth $z$ and the mean infiltration rate $\bar{q}_z$. The general trends are in good agreement to the macrodispersivities expected from linear theory shown in Figure 6. At high infiltration rates, however, the $\alpha_\ast$ values derived from one-particle moments are higher than those derived from theory. As can be seen easily for saturated conditions, the numerical $\alpha_\ast$ values increase faster with travel depth than the analytical ones and reach a plateau that is about 15% higher. The secondary increase near $z = L_z$, however, is not as dramatic. We believe that these discrepancies are caused by the high variability in the velocity field. Without the correction factor $\gamma$ used in equation (20), the difference would even be 50% under saturated conditions at intermediate travel depths.

[38] Figure 9 shows the effective dispersivity $\alpha_e$ representing the expected temporal spread of local concentrations as function of the travel depth $z$ and the mean infiltration rate $\bar{q}_z$. As for the macrodispersivities, the effective dispersivities derived from the two-particle travel time statistics have slightly higher values than those derived from the velocity spectrum shown in Figure 7. Considering that the analytical expression for effective dispersivities, equation (24), is based on a first-order analysis, the overall behavior agrees astonishingly well. It may be noted that the integral in equation (24) is not multiplied by the correction factor $\gamma$ as done in the analytical expressions for macrodispersivities, equations (19) and (20). We exclude this correction factor because this way the results agree better. A more thorough analysis of effective dispersion in highly variable domains will be needed to analyze higher-order effects on effective dispersion.

5.4. Parameterization of Dispersivities

5.4.1. Parametric Models for Macrodispersivity and Effective Dispersivity as Function of Depth and Specific Discharge

[39] A specific objective of the present study is to develop simple expressions approximating the parameters needed in a transfer-function model of transport in the unsaturated zone. These expressions are not derived analytically, nonetheless they reflect basic properties of one- and

Figure 7. Effective dispersivity $\alpha_e$ expected from linear stochastic theory for advective-diffusive transport (equation (24)). Dimensionless graph as function of travel distance and infiltration rate.
two-particle statistics. For the macrodispersivity we use an exponential parametric model:

$$\alpha_\ast(z) = \alpha_\ast^\infty \left(1 - \exp\left(-\frac{z}{\lambda}\right)\right)$$  \hspace{1cm} (42)

in which $\alpha_\ast^\infty$ [m] is the macrodispersivity at the large-time limit, and $\lambda$ [m] is a characteristic length to reach asymptotic behavior. Both $\alpha_\ast^\infty$ and $\lambda$ depend on the mean infiltration rate $q_z$. We fit equation (42) to the apparent macrodispersions $\alpha_\ast(z)$ evaluated from the simulated one-particle variance of travel time $\sigma_1^2(z)$. In order to avoid artifacts related to the periodicity of the velocity field, we restrict the fit to half the domain depth, $0 \leq z \leq L_z/2$.

[40] For the parameterization of effective dispersivities, we make use of the asymptotic analyses of Fiori and Dagan [2000] and Dentz et al. [2000]. At early times, the two-particle covariance of displacements with zero initial separation is identical to the one-particle covariance of displacements, whereas the leading term at large times is $\propto \ln(t)$. In analogy to the one-particle statistics, we choose a model of the two-particle travel time moments that is proportional to the spatial moments at the corresponding mean travel time. We suggest the following parametric model for the spatial gradient of the variogram of two-particle travel time $\gamma_{TT}(z)$:

$$\alpha_e(z) = \alpha_\ast(z) \frac{z}{\kappa + z} = \alpha_\ast^\infty \left(1 - \exp\left(-\frac{z}{\lambda}\right)\right) \frac{z}{\kappa + z}$$  \hspace{1cm} (43)
where $\alpha_\infty$ and $\lambda$ are given from the one-particle moments, and the term $z/(\kappa + z)$ enforces the qualitatively correct behavior at early and large times. Dentz et al. [2000] derived a similar expression as approximation to their analytical results. The parameter $\kappa [m]$ reflects the lag of dilution to catch up with dispersion. We use the following empirical relationships in order to describe the dependence of $\alpha_\infty$, $\lambda$, and $\kappa$ on the mean vertical specific discharge $q_z$:

$$\alpha_\infty(q_z) \approx \alpha_{\text{min}} + \left( \alpha_{\text{max}} - \alpha_{\text{min}} \right) \frac{(q_z)^{n_1}}{(K_\psi)^{n_1} + (q_z)^{n_2}}$$

(44)

$$\lambda(q_z) \approx \lambda_{\text{min}} + (\lambda_{\text{max}} - \lambda_{\text{min}}) \frac{(q_z)^{n_3}}{(K_\psi)^{n_3} + (q_z)^{n_4}}$$

(45)

$$\kappa(q_z) \approx a_\kappa(q_z)^{n_6}$$

(46)

in which the bar of $q_z$ has been omitted for convenience. As fitting criterion for the evaluation of the parameters in equations (44)–(46), we evaluate the average relative deviation of the dispersivities. The parameters approximating $\alpha_\infty(q_z)$ and $\lambda(q_z)$ are determined by fitting the apparent macrodispersivity $\alpha_\psi(q_z)$ in the range $0 \leq z \leq L/2$, and the parameters approximating $\kappa(q_z)$ are determined from the apparent effective dispersivity $\alpha_\psi(q_z)$ over the same range. Optimization is done by a direct search method. The values of $\alpha_{\text{min}}$, $\alpha_{\text{max}}$, $n_1$, $K_\psi$, $\lambda_{\text{min}}$, $\lambda_{\text{max}}$, $n_2$, $K_\lambda$, $a_\kappa$, and $n_6$ are listed in Table 1. The average relative deviation is 7.4% for the macrodispersivity $\alpha_\psi$ and 12.5% for the effective dispersivity $\alpha_\psi$. The highest relative errors occur at the smallest infiltration rates.

Figure 10 shows both $\alpha_\psi(z)$ and $\alpha_\psi(z)$ as calculated by particle tracking in comparison to the parametric model for a mean matrix potential $\psi = -0.3 \, m$. The agreement at smaller travel distances $z$ is excellent, whereas the differences are more pronounced at larger $z$ values because of periodicity. Figure 10 also includes the predictions of linear stochastic theory for macrodispersion and effective dispersion. The slight underestimation of both types of dispersivity by linear theory is clearly visible.

### 5.4.2. Application to Transfer-Function Models of Solute Transport

[42] From the parametric models of unsaturated flow, macrodispersivity and effective dispersivity, we can calculate the statistical moments of one- and two-particle travel times:

$$\mu_\tau(z) = \frac{\sigma_0 S(q_z)}{q_z}$$

(47)

$$\sigma^2_\tau(z) = \frac{2 \mu^2_\tau(z)}{z^2} + 2 \frac{D \mu^3_\tau(z)}{z^2}$$

(48)

$$\gamma_{\tau \tau}(z) = \frac{2 \mu^2_\tau(z)}{z^2} + \frac{2 \mu^3_\tau(z)}{z^2} + \frac{2 D \mu^3_\tau(z)}{z^2}$$

(49)

in which the macroscopic relationship between mean discharge and saturation $S(q_z)$ is given from equations (38)–(40) with $q_z = K(\psi)$. Substituting equation (42) into equation (48) and performing the integration yields the parametric model of the one-particle variance of arrival time:

$$\sigma^2_\tau(z) = \frac{2 \mu^2_\tau(z)}{z^2} + \alpha_\psi \left( z - \lambda \left( 1 - \exp \left( -\frac{z}{\lambda} \right) \right) \right) + \frac{2 D \mu^3_\tau(z)}{z^2}$$

(50)

Analogously, substituting equation (43) into equation (49) and performing the integration yields the parametric model of the two-particle variogram of arrival time:

$$\gamma_{\tau \tau}(z) = \frac{2 \mu^2_\tau(z)}{z^2} + \alpha_\psi \left( z - \lambda \left( 1 - \exp \left( -\frac{z}{\lambda} \right) \right) \right) + \kappa \ln \left( \frac{\kappa}{\kappa + \lambda} \right) + \kappa \exp \left( \frac{1}{\kappa} \left( E_1 \left( \kappa \lambda \right) - E_1 \left( \kappa \lambda - \frac{z}{\lambda} \right) \right) \right) + \frac{2 D \mu^3_\tau(z)}{z^2}$$

(51)

in which $E_1(.)$ is the exponential integral function which may be approximated by equations 5.1.53 and 5.1.54 of Abramovitz and Stegun [1974].

[43] Given the mean $\mu_\tau(z)$ and variance $\sigma^2_\tau(z)$ of the one-particle travel time statistics, an expedient choice of a parametric probability density function of travel times $p(\tau, z)$ is the inverse-Gaussian distribution [Rao et al., 1981]:

$$p(\tau) = \sqrt{\frac{\mu_\tau}{2\pi \sigma_\tau^2 \tau}} \exp \left( -\frac{\mu_\tau(\mu_\tau - \tau)^2}{2\sigma_\tau^2 \tau} \right)$$

(52)

The inverse Gaussian distribution refers to the analytical solution of the advection-dispersion equation with uniform parameters when a Dirac pulse is introduced into the flux and the concentration is measured in the flux. Substituting equation (52) into equation (14) yields a parameterized breakthrough curve of the flux-averaged concentration $c(\tau, z)$ at depth $z$ due to a spatially distributed Dirac-pulse
injection at the surface. The maximum concentration occurs at:
\[ \tau_{\text{max}} = \frac{-3\sigma_t^2 + \sqrt{9\sigma_t^4 + 4\sigma_z^2}}{2\mu_z} \]  

(53)

[44] In order to determine the expected maximum concentration for a point measurement at depth \( z \), we have to replace the one-particle variance of arrival time \( \sigma_t^2(z) \) by the two-particle variogram \( \gamma_{tt}(z) \) in equations (52) and (53). Then, we evaluate \( \rho(\tau) \) at \( \tau_{\text{max}} \) and substitute the result into equation (14). Since \( \gamma_{tt}(z) \) is smaller than \( \sigma_t^2(z) \), the corresponding probability density function of arrival times is more peaked, and the expected maximum concentration for a point measurement is significantly higher than the maximum concentration of the cross-sectionally averaged concentration.

6. Discussion and Conclusions

[45] We have presented a numerical upscaling approach for flow and transport in unsaturated soils under steady-state flow conditions. By choosing a periodic representation of the soil heterogeneities, we have minimized the influence of boundary effects on the macroscopic flow behavior, and by restricting the analysis to gravity-driven flow, we have ensured that the unsaturated conductivity field does not exhibit a unidirectional trend. Therefore the volumetric averages of the saturation \( S \), the potential \( \psi \), and the vertical specific discharge component \( q_z \), determined in our numerical analysis, are unbiased effective parameters. Of course, macroscopic flow in natural unsaturated soils may differ from our description due to transient effects or nonstationary matrix-potential fields, e.g., near the groundwater table. We believe, however, that steady-state gravity-driven flow is relevant in the analysis of transport in the unsaturated zone. At intermediate depths, the temporal fluctuations of water flow are dampened, and gravity is the main driving force of soil water. Particularly, soils undergoing continuous irrigation will tend towards the flow regime analyzed in the present study.

[46] In the present analysis, the fields of unsaturated flow parameters are fully determined by the autocovariance matrix and the correlation among the different parameters at zero separation. In order to create a more realistic picture of unsaturated soil properties, it may be desirable to include structures that cannot be described by two-point statistics such as macro-pores. These type of heterogeneities could be included in the periodic representation of soil parameters. Larger dimensions of the unit cell may be necessary.

[47] Using periodic rather than stationary fields does have an effect on the travel time statistics. The sinusoidal shape of the macrodispersivity \( \alpha(z) \) as function of the travel distance at higher infiltration rates indicates that the size of the unit cell is not large enough for a particle to “forget” its initial position while being transported once through the cell. It should be noted, however, that effects of boundary conditions will occur with any finite approximation of an infinite stationary field. With current computer power on scalar machines, three-dimensional domains will usually be too small to overcome boundary effects, particularly, in the evaluation of higher-order statistics such as multiple-particle moments. In order to minimize the influence of the domain size, we have therefore considered only the moments up to a travel distance of \( L_0/2 \) in the model fitting.

[48] The principal dependence of the macrodispersivity \( \alpha(z) \) on the mean infiltration rate \( q_z \) has already been shown by Roth and Hammel [1996] and Birkholzer and Tsang [1997] for Miller-similar media and discussed more generally by Hammel and Roth [1998]. Our analysis has illustrated that including diffusion leads to diminished macrodispersivities at low infiltration rates. The dependence of the expected temporal spreading of point concentrations, expressed by \( \alpha(z) \), is more complex. The point-related dispersivity \( \alpha(z) \) approaches the value of the macrodispersivity \( \alpha(z) \) at large distances, and therefore larger values of \( \alpha(z) \) would be expected at higher infiltration rates. Conversely, solute dilution needs time to catch up with macrodispersion so that, at a given depth \( z \), the effective dispersivity \( \alpha(z) \) reflecting dilution may be smaller at higher infiltration rates although the corresponding macrodispersivity value is larger.

[49] In the present study, the variability of the unsaturated log conductivity is fairly high. As a consequence, we reach the limit of linear stochastic theories, that predict macrodispersivities and effective dispersivities from the covariance function of the seepage velocity. In order to meet the macrodispersivities obtained by particle tracking, we need to introduce the correction factor \( \gamma' = K_d/K^* \) in the first-order analytical expressions, equations (19) and (20). This has been done and explained earlier by Chin and Wang [1992]. The correction factor is not needed in the first-order approximation of the two-particle covariance of travel time, equation (24). At the current state of knowledge about effective dispersion in highly variable domains, it is unclear whether the good agreement between the prediction by first-order theory and the numerical results is only by chance.

[50] We have developed a parametric model for the dispersivity values describing either, in the case of \( \alpha(z) \), the spreading in the breakthrough curve of the cross-sectionally averaged concentrations or, in the case of \( \alpha(z) \), that of the expected concentrations observed at a point. Using the macroscopic expressions for flow, equations (38)–(40), we can evaluate the mean velocity \( \tau_z \) rather accurately. The two dispersivities used here describe half the rate of change in the spreading of the two concentration types. By substituting parameters \( \alpha(x), \lambda \), and \( \kappa \), derived from equations (44)–(46) into equations (50) and (51) we get the parametric models of the one-particle variance \( \sigma_z^2 \) and two-particle variogram \( \gamma_{zz} \) of travel time which can then be used for the full description of the inverse Gaussian transfer function, equation (52).

[51] One might question the generality of the model describing the dependence on the mean infiltration rate \( q_z \), equations (44)–(46), because it is strictly empirical, particularly for soil textures and spatial patterns of soil properties differing from those considered in the present study. By contrast, the principal dependence on the travel depth \( z \), equations (42) and (43), is based on physical considerations. Even if the curves differ in some details, the principal features are covered by the expressions. Further studies will be necessary to determine the impact of the various parameters describing the heterogeneous fields of unsaturated flow properties on one- and two-particle travel time statis-
CIRPKA AND KITANIDIS: DISPERSION AND DILUTION IN UNSATURATED HETEROGENEOUS MEDIA

Acknowledgments. This study is made possible by the research scholarship “Scaling effects of in-situ mixing in heterogeneous aquifers” of the Deutsche Forschungsgemeinschaft under the grant Ci 26/3-1. Additional funding was provided by EPA through the Western Region Hazardous Substance Research Center, project SU99-9. We thank Iris Stewart for helpful comments.

References

Abrahamowitz, M., and I. A. Stegun (Eds.), Handbook of Mathematical Functions, Dover, Mineola, N.Y., 1974.


O. A. Cirpka, Institut für Wasserbau, Universität Stuttgart, Pfaffenwaldring 61, 70550 Stuttgart, Germany. (olaf.cirpka@iws.uni-stuttgart.de)

P. K. Kitanidis, Department of Civil and Environmental Engineering, Stanford University, Terman Engineering Center, Stanford, CA 94305-4020, USA. (kitanidis@cive.stanford.edu)
Figure 1. Distribution of unsaturated flow parameters in the unit cell (rows 1 and 2) and results of the unsaturated flow calculation at a mean potential $\psi$ of −0.30 m (rows 3 and 4).