

Probability distribution of solute travel time for convective transport in field-scale soils under unsteady and nonuniform flows

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Abstract. This study addresses the development of probability distributions of travel times for one-dimensional (vertical) solute transport in soils. The field-scale soils are considered heterogeneous, with stationary fluctuations of soil hydraulic properties in the horizontal direction but nonstationary fluctuations of these properties in the vertical direction due to layering of the soil, which induces nonstationary heterogeneity. Approximate ensemble probability distribution functions of conservative solute travel time for vertical convective solute transport were derived directly from the convective transport stochastic partial differential equation, under both deterministic and stochastic soil surface water flux (infiltration rate) and under unsteady and nonuniform soil water flows. General depth-varying initial and time-varying boundary conditions were used in these derivations. The magnitude of the approximation in the theoretical probability distribution functions of travel time is quantified mathematically. Utilizing the soil water content data from a University of California, Davis, field site, it is shown that the mathematical condition for this approximation is satisfied for this field. The spatial heterogeneity is represented through a nonstationary soil water content random field which covaries both in time and in space. Dispersion emerges naturally in the derived ensemble probability distribution functions of solute travel time, owing to the stochasticity of soil water content at field scale. Then the theoretical expression for mean solute concentration over a field is derived, by means of the theoretical solute travel time distribution, as a function of time and soil depth, under vertical transport with rectangular pulse solute loading for the upper boundary condition. Comparisons of theoretical probability density functions of solute travel time against their empirical counterparts, obtained from field experimental observations under steady but nonuniform soil water flow, show good agreement. Comparisons of theoretical mean solute concentrations, as they evolve with time and soil depth, against field experimental observations also show good agreement. However, further field experiments under unsteady flow conditions are required for the comprehensive validation of the developed theory.

Introduction

Many situations exist where groundwater has become contaminated by agricultural and industrial chemicals. Quantification of the risks of solute concentrations in time and space within the vadose zone would quantify the effectiveness of various alternatives for the abatement of pollution in field soils and receiving groundwaters. Quantification of risks due to solute concentrations can best be accomplished by the development of the probability distributions of solute travel times

and concentrations as solute plumes evolve in time and space within field-scale soils.

Nielsen et al. [1972] have demonstrated by experiments that even a 150-ha field which is fairly uniform in the horizontal direction ("fairly uniform soil classification") has large variations in the hydraulic conductivity values and in infiltration rates from location to location. Hence this study established the fact that at field scale the moisture flows in the vadose zone can best be modeled as a stochastic process. On the basis of solute application experiments at the same field, *Biggar and Nielsen* [1976, p. 82] concluded that "the position of a solute within a soil profile even within a relatively small area or plot is... difficult to ascertain." *Jury* [1982, p. 363] states that "... many causes of spatial variability of water and solute transport... render measurement of the hydraulic and retention parameters of a field soil all but impossible. As a consequence, the deterministic approach to modeling chemical transport is abandoned..." Citing the results of *Nielsen et al.* [1972] and *Biggar and Nielsen* [1976], *Dagan and Bresler* [1979] and *Bresler and Dagan* [1979] considered the field-scale solute transport as a stochastic process. The stochastic approach to treating field-scale solute transport in soils was later followed

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by Bresler and Dagan [1981, 1983], Jury [1982], Jury *et al.* [1982], Simmons [1982], Sposito *et al.* [1986], Russo [1991], Russo and Dagan [1991], Destouni [1992], Jury and Scotter [1994], and others.

Dagan and Bresler [1979] and Bresler and Dagan [1979] have demonstrated that "pore scale hydrodynamic dispersion has a negligible effect as compared with field scale dispersion caused by field heterogeneity and that convection by average flow velocity coupled with heterogeneity is the main mechanism which governs the solute spreading in the field" [Bresler and Dagan, 1979, p. 468]. They have shown that "for the Panoche soil solute spread due to field heterogeneity is much larger than the spread caused by the conventional pore-scale hydrodynamic dispersion so that the latter can be safely neglected" [Bresler and Dagan, 1979, p. 472]. Therefore they were first in considering solute transport in field-scale soils as a purely convective stochastic phenomenon due to soil heterogeneity. They conceptualized leaching over a heterogeneous field as a collection of depth-wise homogeneous vertical columns, with statistically independent hydraulic properties varying in the x - y horizontal plane over field locations, depending upon the local soil properties. They assumed steady state infiltration conditions (with steady and uniform flow velocity and water content) for each hypothetical column. Saturated hydraulic conductivity K_s (taken lognormally distributed and representing the effect of field-scale soil heterogeneity) and steady recharge rate R (as upper boundary condition for soil moisture flows and taken to be uniformly distributed) were considered to be stochasticity sources. Hence they solved the field-scale conservative solute transport in the vadose zone as a stochastic convective vertical solute transport under steady, uniform stochastic flow conditions (due to randomness of K_s and R) with zero concentration initial conditions (IC) and step input concentration (C) upper boundary condition (UBC). Under this framework they were the first to develop analytical solutions for the probability density function (pdf) and average of solute concentration.

Following the work of Dagan and Bresler [1979], Simmons [1982], Jury [1982], Destouni [1992], and Jury and Scotter [1994] also conceptualized field-scale solute transport in soils as a stochastic convective phenomenon. Simmons [1982] formulated a stochastic convective transport model for vertical field-scale conservative solute transport in a single field-scale column, as opposed to an ensemble of vertical soil columns over a field, as considered by Dagan and Bresler [1979]. Simmons was the first to give a mathematical justification of the convective solute transport equation by showing that the equation follows directly from the solute mass continuity and soil water continuity equations. He described vertical field-scale solute transport by the ensemble pdf of solute travel time in this single field-scale column. In contrast to the steady state, uniform flow field of Dagan and Bresler [1979], Simmons [1982] considered a steady state but nonuniform stochastic flow field for solute transport. He considered zero concentration IC and instantaneous pulse and rectangular pulse solute loads as UBCs. Instead of deriving the ensemble pdf of travel time from the convective solute transport equation, Simmons assumed a Fickian pdf (in terms of a convection-dispersion equation with constant coefficients for average concentration) and a lognormal pdf for the travel time. He then obtained the travel time moments from these assumed pdfs. However, later in his paper, Simmons [1982, p. 1206] stated that "A complexity of the ensemble approach is that the travel time pdf must be known

or obtained for the underlying stochastic velocity. Here a well-known pdf was assumed."

Taking a stochastic convective approach to vertical solute transport in soils, Jury [1982] proposed a transfer function model for simulating solute transport under natural field conditions. This approach measures the distribution of solute travel times from the soil surface to a reference depth. Then using this distribution function and accounting for uncertainty in water application rates (input water flux rates) and in solute travel times due to field-scale soil heterogeneity, Jury derived the average solute concentration as functions of time and soil depth under zero concentration IC and step input and rectangular pulse input as UBCs. The transfer function model of Jury [1982] was tested by a field experiment by Jury *et al.* [1982]. Good agreement was found between the predicted (after the transfer function model was calibrated) and measured values of solute concentration at various soil depths. Recently, Jury and Scotter [1994] considered stochastic convective nonreactive solute transport by steady flow within a vertically homogeneous but horizontally heterogeneous field soil. They considered soil water content and soil water flux conditions to be constant (uniform) in the vertical flow direction locally but random in the horizontal directions at field scale. They then developed a new theory which relates the travel time probability density function (pdf) with travel distance pdf. The novelty of their approach is that "Single observation of a travel time or travel distance pdf is the only calibration required to formulate and solve" solute transport problems at field soils under both initial and boundary conditions [Jury and Scotter, 1994, p. 1333].

Destouni [1992] used the same conceptualization of Dagan and Bresler [1979] but incorporated vertical soil heterogeneity into the vertical solute transport model by averaging the saturated hydraulic conductivity vertically at each point in the field. Therefore she considered field-scale vertical solute transport by a steady state but nonuniform flow field under zero solute concentration IC and instantaneous (and areally uniformly distributed) pulse input UBC. She analyzed the evolution of the field-scale breakthrough curve as a function of depth in terms of the first two moments of solute travel time.

While the above mentioned studies have established the fundamental stochastic convective nature of solute transport at field-scale soils, Butters and Jury [1989] and Russo [1991] established the essentially one-dimensional vertical nature of this transport and the importance of vertical soil heterogeneity on this transport. The two-dimensional numerical simulation studies of water flow and solute transport on a heterogeneous vertical soil plane (in x - z directions) by Russo [1991] showed no apparent horizontal solute spreading, while the location of the center of solute mass and the spread around the center of mass in the vertical direction varied considerably in time, thereby justifying the one-dimensional transport models of the above mentioned studies. The numerical experiment of Russo [1991] showed that the correlation scale of solute concentrations in the horizontal direction is around 1 m, thereby justifying the independent columns hypothesis of Dagan and Bresler [1979]. Russo [1991] also showed, by means of spatial moment analysis, that the effective vertical solute velocity has a clear time trend, thus pointing to the timewise nonstationary nature of solute transport. Stressing the fundamentally transient nature of soil water flows, Russo [1991, p. 268] stated that "under both natural and irrigated agricultural conditions the water flow in the vadose zone is affected by time-dependent processes which act on the soil surface." With respect to the effect

of soil heterogeneity in the vertical direction on solute transport, he stated (p. 279) that "relatively small variations in the soil hydraulic properties normal to the direction of flow can exert a significant influence on the spread of the solute plume."

In the light of above mentioned studies, this study addresses the development of ensemble probability distribution functions of travel times for stochastic time-depth nonstationary (but horizontally stationary) field-scale, vertical convective, conservative solute transport. The time-depth evolutionary probability distribution functions of solute travel times are developed directly from the convective solute transport equation under unsteady and nonuniform soil water flows with their corresponding ICs and UBCs, and under time-varying solute concentration UBCs and depth-varying solute concentration ICs. However, as will be shown, in the derivation of the ensemble probability distributions of solute travel time, only the depth-varying ICs and time-varying UBCs of soil water flow need to be considered. Utilizing the analytical continuum solution from the convective conservative transport equation for the solute front, the time-soil depth evolving ensemble cumulative distribution function (CDF) and ensemble probability density function (pdf) of conservative solute travel time are obtained. The soil surface water flux (infiltration rate), although considered generally as time varying in the solutions, is first considered as deterministic. Then the theoretical time-soil depth evolving probability distribution of solute travel times is generalized to the case of both stochastic porous media and stochastic soil surface water flux (infiltration rate).

In the final section, for the verification of theoretical results, comparisons of theoretical probability density functions of solute travel times are made against their empirical counterparts, obtained from field experimental observations under steady but nonuniform soil water flow and unsteady solute transport. Also, comparisons of theoretical mean solute concentrations, as they evolve with time and soil depth, are performed against field experimental observations.

Derivation of Time-Depth Evolving Probability Distributions of Conservative Solute Travel Times

The convective vertical transport equation for a conservative solute through a vertically heterogeneous soil by unsteady and nonuniform soil water flow is expressed as [Simmons, 1982]

$$\frac{\partial \theta C}{\partial t} + \frac{\partial q C}{\partial z} = 0 \quad (1a)$$

where C denotes time-depth dependent solute concentration, z is depth coordinate (positive downward), t is time, q is local Darcy flux in the vertical direction, and θ is the local volumetric water content. The continuity equation for the vertical water flow (of constant density) in the unsaturated zone may be expressed by

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} = 0 \quad (1b)$$

Combining (1a) and (1b), the solute vertical convective transport equation by unsteady and nonuniform soil water flow reduces to [Simmons, 1982]

$$\frac{\partial C(z, t)}{\partial t} + \frac{q(z, t)}{\theta(z, t)} \frac{\partial C(z, t)}{\partial z} = 0 \quad (1c)$$

In (1c) it is assumed that the solid (soil) and liquid phase are incompressible. It is also assumed that the water table is sufficiently deep so that it does not have significant influence on flow in the vadose zone, thereby leading to the assumption of a semi-infinite porous medium. The initial condition (IC) and upper boundary condition (UBC) for soil water flow are

$$\text{IC} \quad \theta(z, 0) = \theta_n(z) \quad z > 0 \quad (2a)$$

$$\text{UBC} \quad q(0, t) = q_0(t) \quad t > 0 \quad (2b)$$

and the conditions for solute transport are

$$\text{IC} \quad C(z, 0) = C_n(z) \quad z > 0 \quad (2c)$$

$$\text{UBC} \quad C(0, t) = C_0(t) \quad t > 0. \quad (2d)$$

From vertical convective transport equation (1c) the equation of the characteristic was obtained by Wilson and Gelhar [1981] and by Smiles *et al.* [1981] as

$$u(z, t) = \int_0^z \theta(\xi, t) \partial \xi - \int_0^t q(0, \tau) \partial \tau = \gamma \quad (3)$$

where γ is an arbitrary constant. The location of the solute front center of mass was then obtained by Wilson and Gelhar [1981] and by Smiles *et al.* [1981] by setting $u(z, t) = 0$. The curve $u(z, t) = 0$ partitions the z - t space into two regions: one where the solution is dictated by the initial condition and the other where the solution is determined by the boundary condition. Thus $u(z, t) = 0$ is tantamount to locating the position of a solute particle which is being advected by the flow field.

From above it follows that given a particular realization of the soil water content process, the time $T(z)$ that it takes a solute particle (which is injected at the soil surface $z = 0$ at time $t = 0$) to reach soil depth z (by vertical convective transport), being less than some fixed time t , is equivalent to

$$\int_0^z \theta(\xi, t) \partial \xi < \int_0^t q(0, \tau) \partial \tau \quad (4)$$

where the left-hand side of (4) is the soil water storage volume $\Phi(z, t)$, i.e.,

$$\Phi(z, t) = \int_0^z \theta(\xi, t) \partial \xi. \quad (5)$$

The right-hand side of (4) is the cumulative infiltration, $Q(t)$, into the soil since the initial time, i.e.,

$$Q(t) = \int_0^t q(0, \tau) \partial \tau. \quad (6)$$

The argument of the integral in (6), $q(0, \tau)$, is the soil surface water flux, or the infiltration rate. These two terms will be used interchangeably throughout the paper.

The solute travel time to a depth z being less than some specified time t means that the convective solute front has already surpassed the depth z before time t . In terms of the soil water flow dynamics, this means that the cumulative infiltration at time t , to a soil column of unit cross-sectional area, has exceeded the soil water storage at time t to a depth z in that soil column. This condition is expressed by (4).

As may be seen from (5), the soil water storage $\Phi(z, t)$ is an

explicit function of the soil water content θ . Meanwhile, the cumulative infiltration $Q(t)$ depends upon both the soil water content and the water application rate. In this study the field-scale soils are considered heterogeneous with stationary fluctuations of soil hydraulic properties in the horizontal direction but nonstationary fluctuations of these properties in the vertical direction due to layering of the soil. Consequently, the water content θ is a random field in time and space, and the soil water storage $\Phi(z, t)$ becomes a random function over a field-scale soil. Owing to the assumption of stationarity in the horizontal direction, the (marginal) probability distribution of $\Phi(z, t)$ will remain the same along the horizontal extent over a field soil. However, from (5) it follows that this distribution will vary as a function of soil depth, as will be shown in the following. Under transient water flow conditions (time nonstationarity), this distribution will also vary with time. Since the infiltration rate will fluctuate randomly over a field soil due to soil heterogeneity even if the water application rate is uniform over the field, the cumulative infiltration $Q(t)$ will also become a random function over a field soil. Under the assumption of stationary soil heterogeneity in the horizontal directions, its pdf will remain the same along these directions over a field soil. Under these considerations the solute travel time $T(z)$ becomes a stationary random function along the horizontal extent over a field soil. Therefore its (univariate) pdf will be the same along the horizontal directions. However, its pdf will change as a function of soil depth, as will be shown in the following.

From (4) it follows that the cumulative distribution function (CDF) for the solute travel time to any soil depth z is obtained as

$$P[T(z) < t | Q(t)] = P[\Phi(z, t) < Q(t)]. \quad (7)$$

The conditioning on the left-hand side of (7) is shown in order to indicate that the time-varying soil surface water flux and hence the cumulative infiltration are given deterministically. It is evident from (4)–(7) that the solute travel time CDF is expressed in terms of the soil water content $\theta(z, t)$ and of the soil surface water flux (infiltration rate) $q(0, t)$. Therefore in order to obtain an explicit expression for the probability distribution function of solute travel times directly from the convective transport equation (1c), it is necessary to satisfy the soil water flow conditions (2a) and (2b). From (7) it also follows that in order to obtain the CDF of $T(z)$ within the framework of (1c), (2a), and (2b), it is only necessary to derive the probability distribution function of the soil water storage volume $\Phi(z, t)$.

It is important to note here that since both $\Phi(z, t)$ and $Q(t)$ are dependent upon the soil water content θ , they are correlated. Fundamentally, even if $Q(t)$ is given in (7), the probability distribution of $\Phi(z, t)$ will be conditional upon $Q(t)$. In order to obtain this distribution of Φ conditional upon Q , it is necessary to derive first the bivariate probability density function (pdf) of Φ and Q from soil water dynamics. Such a pdf is yet to be derived from physical considerations and would necessitate a difficult study in soil water dynamics where one would have to solve first for the joint pdf of the soil water content and infiltration rate. Only after such a joint pdf is obtained from soil water conservation laws can one obtain the desired joint pdf of soil water storage and cumulative infiltration. Since our study is focused on the transport phenomena of solutes, we instead make the approximation of independence between Φ and Q so that once Q is given, the probability $P[\Phi(z, t) < Q(t)]$ will be obtained directly from the uncon-

ditional probability distribution of $\Phi(z, t)$. However, by means of (5) the probability distribution of soil water storage will be obtained explicitly in terms of the statistical properties of the soil water content θ , which also influences the behavior of $Q(t)$.

Equation (5) may be interpreted as a stochastic integral equation, since θ is a random field. Then one obtains from (5) the stochastic differential equation

$$\frac{\partial \Phi}{\partial z} = \theta(z, t) \quad (8)$$

From (8) it follows that in the Φ phase space the conservation of mass yields (see *van Kampen* [1976] or *Kavvas and Govindaraju* [1991] for details about conservation of mass in phase spaces)

$$\frac{\partial \rho(\Phi; z, t)}{\partial z} = -\theta(z, t) \frac{\partial \rho(\Phi; z, t)}{\partial \Phi} \quad (9)$$

since (8) determines velocity (with respect to z) at each point of Φ phase space. Because $\theta(z, t)$ is a random field, (9) is a stochastic partial differential equation (PDE). In (9), ρ is the stochastic mass density in the Φ phase space. It is seen from (9) that ρ evolves with Φ and z . From *van Kampen's* [1976] lemma, it follows that the pdf of $\Phi(z, t)$ is expressed by

$$P(\Phi; z, t) = \langle \rho(\Phi; z, t) \rangle \quad (10)$$

where angle brackets denote the ensemble averaging operator. Therefore in order to obtain the evolution equation for the pdf of $\Phi(z, t)$ from (9), it is necessary to take the ensemble average of the stochastic partial differential equation (9).

Define the deterministic operator $A_0(t, z)$ and the stochastic operator $\alpha A_1(t, z)$ by

$$A_0(t, z) = -\langle \theta(z, t) \rangle \frac{\partial}{\partial \Phi} \quad (11a)$$

$$\alpha A_1(t, z) = [-\theta(z, t) + \langle \theta(z, t) \rangle] \frac{\partial}{\partial \Phi} \quad (11b)$$

In terms of (11a) and (11b) the stochastic PDE (9) may be rewritten as a stochastic operator ordinary differential equation (ODE):

$$\frac{\partial \rho}{\partial z} = [A_0(t, z) + \alpha A_1(t, z)] \rho \quad (12)$$

where in this context, α^2 may be interpreted as $\text{Var}[\theta(z, t)]$. Utilizing the cumulant expansion solutions of *Kubo* [1963] and *van Kampen* [1974] in nonstationary stochastic initial value problems, *Kavvas et al.* [1993] have given the ensemble average of (12) to order $\alpha^2 z_c$, where z_c is the correlation length of $\alpha A_1(t, z)$ and thereby of $\theta(z, t)$ (in slightly modified notation for this context in terms of depth z instead of time t),

$$\begin{aligned} \frac{\partial \langle \rho(\Phi; z, t) \rangle}{\partial z} &= A_0(t, z) \langle \rho(\Phi; z, t) \rangle + \alpha^2 \int_0^z d\xi \\ &\cdot \left\langle \left\langle \left\langle A_1(t, z) \exp \left(\int_{z-\xi}^z A_0(t, s) ds \right) A_1(t, z-\xi) \right\rangle \right\rangle \right\rangle \\ &\cdot \exp \left(- \int_{z-\xi}^z A_0(t, s) ds \right) \langle \rho(\Phi; z, t) \rangle \end{aligned} \quad (13a)$$

where

$$\exp \left(\int_0^z X(s) ds \right) = 1 + \sum_{m=1}^{\infty} \int_0^z ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{m-1}} ds_m X(s_m) \cdots X(s_1) \quad (13b)$$

is the chronologically ordered exponential for depths $z > s_1 > s_2 > \cdots > s_{m-1} > s_m > 0$ for any dummy function X . The following inverse relationship holds for (13b):

$$\left[\exp \left(\int_0^z X(s) ds \right) \right]^{-1} = \exp \left(\int_0^z -X(s) ds \right) \quad (13c)$$

Also, the notation $\langle\langle \cdot \rangle\rangle$ denotes the depth-ordered second cumulant (covariance) operator [see *van Kampen*, 1974], which is defined for a noncommutative operator $X(z)$ by

$$\langle\langle X(z)X(s_1) \rangle\rangle = \langle X(z)X(s_1) \rangle - \langle X(z) \rangle \langle X(s_1) \rangle \quad (13d)$$

for soil depths $z > s_1$. Performing the operations dictated by operators A_0 and A_1 on (13a) and utilizing the identity in (10), one obtains from (13a) the following Fokker-Planck equation (FPE) for the evolution of pdf $P(\Phi; z, t)$ of soil water storage (see the appendix):

$$\frac{\partial P(\Phi; z, t)}{\partial z} = -\langle \theta(z, t) \rangle \frac{\partial P(\Phi; z, t)}{\partial \Phi} + \int_0^z d\xi \text{Cov} [\theta(z, t); \theta(z - \xi, t)] \frac{\partial^2 P(\Phi; z, t)}{\partial \Phi^2} \quad (14a)$$

to order $\alpha^2 z_c$. One may note from (14a) that for the ensemble pdf of $\Phi(z, t)$ (and thereby of solute travel times through (7)) at field plot scale, the dispersion appears naturally in the Fokker-Planck equation for $P(\Phi; z, t)$, owing to field heterogeneity, as manifested by the spatial covariance of the soil water content, although only the convective solute transport equation is being considered here.

Since the above Fokker-Planck equation for the evolution of the probability density function (pdf) of Φ is a deterministic partial differential equation (PDE) in the independent variables z and Φ , it is necessary to develop the initial and boundary conditions for this PDE in order to solve it for $P(\Phi; z, t)$. Remembering that $\Phi(z, t)$ is the water storage volume for a soil column of depth z and unit horizontal area at time t , the initial condition may be determined as follows. Since z replaces the conventional time variable t as one of the independent variables in (14a), the initial condition (IC) corresponds to $z = 0$. When $z = 0$, the depth of soil is zero, and hence there can be no moisture in the soil column of depth zero. Therefore the initial condition (IC) is stated as

$$\text{IC} \quad P(\Phi; 0, t) = \delta_+(\Phi) \quad \Phi \geq 0, t > 0 \quad (14b)$$

which means $\Phi(0, t) = 0$ in probabilistic terms. In (14b), $\delta_+(\cdot)$ is the Dirac delta function on the nonnegative real line. For the boundary conditions, all of the probability mass needs to be distributed in the Φ interval between $\Phi = 0$ and $\Phi = +\infty$, since the water in a soil column is a nonnegative quantity. If the probability mass is to be contained in the Φ interval $(0, +\infty)$, there should be a reflecting barrier upper boundary condition

(UBC) at $\Phi = 0$. Such a condition shall correspond to setting the probability current J in the Φ phase space equal to zero. That is,

$$J(\Phi; z, t)|_{\Phi=0} = 0.$$

Therefore the no-flux upper boundary condition may be stated as

$$J(\Phi; z, t)|_{\Phi=0} = -a(z, t)P(\Phi; z, t) + b(z, t) \frac{\partial P}{\partial \Phi} \Big|_{\Phi=0} = 0 \quad z > 0, t > 0 \quad (14c)$$

where $a(z, t)$ and $b(z, t)$ are defined as follows:

$$a(z, t) = -\langle \theta(z, t) \rangle \quad (15)$$

$$b(z, t) = \int_0^z d\xi \text{Cov} \{ \theta(z, t); \theta(z - \xi, t) \}.$$

The lower boundary condition at $\Phi = +\infty$ could correspond to setting $J(+\infty; z, t) = 0$. However, a more useful condition to use is the so-called compatibility condition, which conserves the probability mass within the Φ interval $(0, +\infty)$. Hence the compatibility condition is stated as

$$\int_0^{\infty} P(\Phi; z, t) d\Phi = 1 \quad (14d')$$

which assures that the solution of the FPE in (14a) under the conditions (14b) and (14c) is a probability density function and that all the probability mass is in $(0, +\infty)$.

There is no known explicit solution to the partial differential equation system (14a), (14b), (14c), and (14d'). The difficulty in obtaining the exact explicit solution for this system is due to the upper boundary being a moving boundary. However, one can consider a free boundary condition

$$P(\pm\infty; z, t) = 0 \quad (14e')$$

instead of (14c) and consider a Φ interval of $(-\infty, +\infty)$ instead of the actual Φ interval of $(0, +\infty)$. Then one can obtain the explicit solution for the FPE (14a) under (14b), (14d'), and (14e')

$$P(\Phi; z, t) = \frac{1}{\sqrt{4\pi B(z, t)}} \exp \left\{ -\frac{1}{2} \frac{[\Phi - G(z, t)]^2}{2B(z, t)} \right\} \quad z \geq 0 \quad \Phi \geq 0 \quad (16a)$$

where

$$B(z, t) = \int_0^z du \int_0^u d\xi \text{Cov} [\theta(u, t); \theta(u - \xi, t)] \quad (16b)$$

$$G(z, t) = \int_0^z \langle \theta(\xi, t) \rangle d\xi = \langle \Phi(z, t) \rangle \quad (16c)$$

This solution is valid to order $z_c \text{Var} [\theta(z, t)]$. This means that the derived Gaussian distribution for the soil water storage Φ is only valid to the order of the covariance of the soil water content random field. That is, this distribution will be valid only in those field conditions where the third- and higher-order cumulants of the soil water content random field are

small with respect to the covariance of the water content. Recently, Kavvas *et al.* [1995] have shown by numerical Monte Carlo experiments that the Gaussian distribution for Φ is plausible as a first approximation. Furthermore, this Gaussian distribution does not satisfy the no-flux upper boundary condition (14c) of the Fokker-Planck equation (14a), which resulted from the cumulant expansion to the order of the covariance of the soil water content. The effect of ignoring this boundary condition will be explored in the following. It is seen that the approximate Gaussian pdf (16a) has mean $G(z, t)$ as a depth-wise integral of the mean soil water content and has variance $2B(z, t)$, described in terms of the covariance function of θ random field. This means that this Gaussian distribution is described explicitly in terms of the mean and covariance statistical properties of the soil water content and will vary with soil depth z and time t . Hence this distribution establishes that, in general, the soil water storage is a time-depth nonstationary random function.

Since this approximate Gaussian solution will not satisfy (14c), based upon this solution, some probability mass will leak to the Φ interval $(-\infty, 0)$. Therefore it is necessary to calculate how much probability mass leaks to $(-\infty, 0)$ in order to assess the magnitude of the error committed by the approximate solution. Since (16a) is a Gaussian pdf, from a standard Gaussian probability table it may be seen that under the condition

$$\frac{G(z, t)}{\sqrt{2B(z, t)}} \geq 2.33 \quad (17)$$

only 1% of the probability mass can leak to the Φ region $(-\infty, 0)$. In other words, under the condition (17) one makes an error of 1% probability by using the solution (16a), which ignores the no-flux boundary condition (14b). Meanwhile, for the condition

$$\frac{G(z, t)}{\sqrt{2B(z, t)}} \geq 4 \quad (18)$$

only 0.000001 probability mass can leak to the Φ region $(-\infty, 0)$. Hence under the condition (18) one makes an error of 0.0001% probability by using the solution (16a), which ignores the no-flux boundary condition (14c). Consequently, for all practical purposes, once the $\theta(z, t)$ random field satisfies (18), the approximate solution (16a) may be considered an exact solution to the actual problem of (14a), (14b), (14c), and (14d'). In fact, even when only the less strict condition (17) is satisfied, the solution (16a) may be considered to be a very good approximation to the solution of (14a), (14b), (14c), and (14d'). In the application section the practicality of the conditions (17) and (18) shall be explored in terms of field data.

Combining (16a) with (7), the approximate ensemble CDF of conservative solute travel times, which is obtained directly from the vertical convective solute transport equation (1c) under the general unsteady and nonuniform soil water flow conditions (2a) and (2b), is expressed as

$$P[T(z) < t | Q(t)] = F_\Phi(Q(t))$$

$$= S \left(\frac{Q(t) - \int_0^z \langle \theta(\xi, t) \rangle d\xi}{\sqrt{2 \int_0^z du \int_0^u d\xi \text{Cov}[\theta(u, t); \theta(u - \xi, t)]}} \right) \quad (19)$$

to order $z_c \text{Var}[\theta(z, t)]$. In (19), F_Φ denotes the CDF of $\Phi(z, t)$, while $S(\cdot)$ is the CDF of a standard Gaussian (normal) random variable. It follows from the above discussion for the pdf of $\Phi(z, t)$ that when the condition (18) is satisfied, the expression (19) may be considered an almost exact CDF of solute travel times to order $z_c \text{Var}[\theta(z, t)]$. When the less restrictive condition (17) is satisfied, the expression (19) may be considered to be a good approximation (with 1% probability error) to the true CDF of solute travel times under (1c), (2a), and (2b) to order $z_c \text{Var}[\theta(z, t)]$. Expression (19) shows clearly that solute travel time CDF depends upon the infiltration rate $q(0, t)$ and on the mean and covariance behavior of the soil water content random field. It may be pointed out that in (19), $q(0, t)$ is deterministic. Its randomization shall be dealt with later. Although the probability distribution of solute travel times looks as if it is Gaussian, it actually is not. The pdf of solute travel time, $f_{T(z)}(t)$, is obtained from (19) as

$$\begin{aligned} f_{T(z)}[t | Q(t)] &= dF_\Phi[Q(t)]/dt = P[Q(t), z, t]q(0, t) \\ &= \frac{1}{\sqrt{4\pi B(z, t)}} \exp \left\{ -\frac{1}{2} \frac{[Q(t) - G(z, t)]^2}{2B(z, t)} \right\} q(0, t) \quad (20) \\ & \quad z > 0 \quad t > 0 \end{aligned}$$

to order $z_c \text{Var}[\theta(z, t)]$. Hence from (20) it follows that although the approximate pdf $P(\Phi, z, t)$ of $\Phi(z, t)$ is Gaussian, as long as the infiltration rate (soil surface water flux) $q(0, t)$ varies with time t , the pdf of the solute travel time will be non-Gaussian.

Finally, the more general case, when $q(0, t)$ is also taken as stochastic in addition to the stochasticity due to soil heterogeneity, is considered. The solute travel time CDF under stochastic soil surface water flux (stochastic infiltration rate) follows from (19) as

$$\begin{aligned} P[T(z) < t] &= \int P[T(z) < t | Q(t)] f(Q(t)) dQ(t) \\ &= \int S \left(\frac{Q(t) - \int_0^z \langle \theta(\xi, t) \rangle d\xi}{\sqrt{2 \int_0^z du \int_0^u d\xi \text{Cov}[\theta(u, t); \theta(u - \xi, t)]}} \right) \\ & \quad \cdot f[Q(t)] dQ(t) \quad (21) \end{aligned}$$

to order $z_c \text{Var}[\theta(z, t)]$ and where $f(Q(t))$ is the pdf of $Q(t)$.

Mean Solute Concentration Under Rectangular Pulse Solute Loading

Once the CDF of solute travel time $P[T(z) < t]$ is derived, as in (21), it is then possible to obtain the theoretical expression of mean solute concentration for vertical convective transport under rectangular pulse solute loading as a surface boundary condition. In mathematical terms the initial and boundary conditions for this case are (2a) and (2b) for soil water flows, and

$$IC \quad C(z, 0) = 0 \quad z > 0 \quad (22a)$$

$$\text{UBC} \quad C(0, t) = c_0[H(t) - H(t - t_0)] \quad t > 0 \quad (22b)$$

for solute transport [Simmons, 1982]. In (22a) and (22b), c_0 is the surface solute concentration, t_0 is the duration of solute pulse, and H is the step function, defined by

$$\begin{aligned} H(\alpha) &= 1 & \alpha > 0 \\ H(\alpha) &= 0 & \alpha \leq 0. \end{aligned} \quad (23)$$

Under (1c), (2a), (2b), (22a), and (22b), the solute concentration is expressed as

$$C(z, t) = c_0 H[t - T(z)] \quad 0 < t \leq t_0 \quad (24)$$

$$C(z, t) = c_0 [H(t - T(z)) - H(t - t_0 - T(z))] \quad t > t_0.$$

Taking expectations on both sides of (24), the mean concentration $\langle C(z, t) \rangle$ is obtained as

$$\langle C(z, t) \rangle = c_0 \{P[T(z) < t]\} \quad 0 < t \leq t_0 \quad (25a)$$

$$\langle C(z, t) \rangle = c_0 \{P[T(z) < t] - P[T(z) < t - t_0]\} \quad (25b)$$

$$t > t_0$$

given that the duration t_0 of the rectangular solute pulse in time is deterministically known. Expression (25b) was developed first by Simmons [1982].

However, in field experiments, t_0 often varies randomly over the field due to randomly varying infiltration rates. Therefore for field conditions, (25) is generalized to

$$\begin{aligned} \langle C(z, t) \rangle &= c_0 \int_0^t \{P[T(z) < t] - P[T(z) < t - t_0]\} f(t_0) dt_0 \\ &+ c_0 P[T(z) < t] P[t_0 \geq t] \end{aligned} \quad (26)$$

where $f(t_0)$ is the probability density of the random duration t_0 , and $P[t_0 \geq t]$ is the probability that the random duration t_0 of the rectangular solute pulse is greater than or equal to a specified time t .

Model Testing

In this section the objective is to first explore the validity of the approximate solution (16a), which was developed above for the pdf of soil water storage volume $\Phi(z, t)$. This solution, in turn, determines the CDF and pdf of solute travel time $T(z)$ through (19) and (20). It is clear from (16a), (16b), and (16c) that the solution for the pdf of $\Phi(z, t)$ depends basically on the mean and the covariance behavior of the soil water content random field $\theta(z, t)$. Since the theoretical modeling of the mean and covariance functions of $\theta(z, t)$ is outside the scope of this study, these functions were constructed based on the field data from a field site at University of California, Davis. The field plot was divided into 24 subplots, each of which is 2.5 m by 2.5 m and isolated from the others by small dikes. Chloride has been chosen as the conservative tracer for the solute transport experiments. The soil water content was measured using a neutron probe at eight different depths (15, 30, 45, 60, 120, 180, 240, and 300 cm). In order to monitor solute movement, each subplot was instrumented with 12 sets of TDR (time domain reflectometry) rods to depths ranging from 15 to 45 cm and with 12 sets of solution samplers ranging in depth from 30 to 300 cm. The subplots were ponded and allowed to

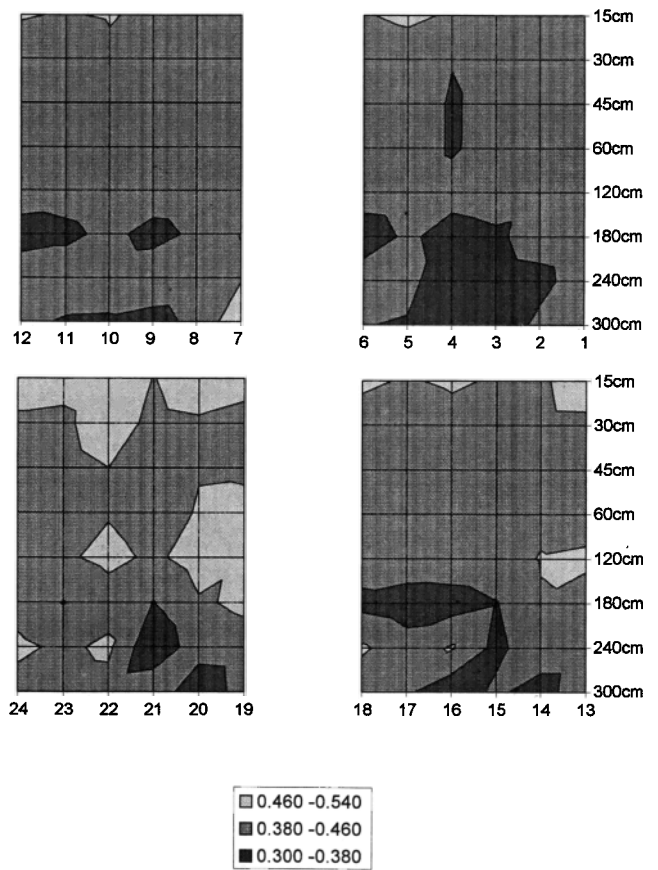


Figure 1. Soil water content distribution observed over the 24 subplots of the experimental field under the steady state flow.

reach steady state water flow throughout the 300-cm profile. The steady infiltration rate for each plot was measured by rate of drop of the ponded water height. Figure 1 shows the soil water content distribution observed over the 24 subplots under this steady state. The chloride was then applied over the field simultaneously as a rectangular pulse. Water was then ponded on the surface continually, and the transport of the chloride pulse was monitored for 3 weeks. Total mass and concentration of applied chloride in each subplot were the same. However, durations of each pulse were not the same due to different infiltration rates in each subplot. The plot infiltration rate could be used to develop the UBC water flux if the ponded infiltration rate was uniform within the plot. This is highly unlikely. Measurements of local-scale water infiltration rate would be preferred but are not measurable in a ponded plot. However, an estimate of the local-scale infiltration rate may be determined from the relative conductivity measured from the individual TDR rods within the plots at the time the solute pulse has completely entered the surface soil. The amount of solute residing in the top 15 cm of soil, represented by each TDR probe, is directly proportional to the surface water flux. To determine the fraction of the solute that has entered a particular location, the electrical conductivity (EC) of the resident soil water is compared to the EC of the soil water if the surface water flux were uniform. Given a number of probes, the ratio of the local change in EC to the average change in EC, calculated using all probes, will yield a relative local solute

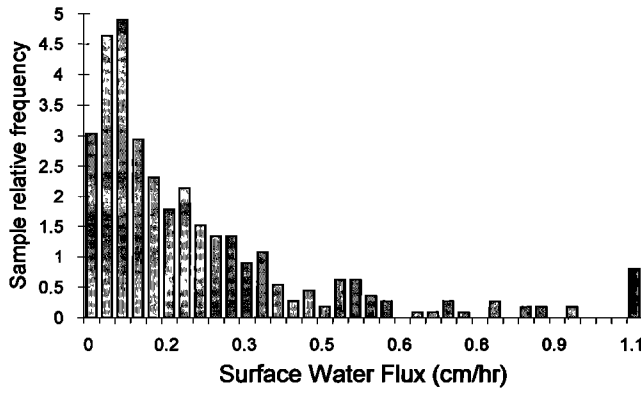


Figure 2. Sample relative frequency histogram of the surface water flux observed in the experimental field.

amount. The product of the relative local solute amount at any TDR location and the plot infiltration rate gives a relative infiltration rate at each TDR location. The pdf of these local-scale infiltration rates is considered a more realistic measure of the field-scale variability for the UBC than would the pdf of the plot infiltration rate. Figure 2 shows the observed pdf (sample relative frequency histogram) of the infiltration rate (soil surface water flux). Solute travel times were determined from TDR measurements by the method of moments as described by Kachanoski *et al.* [1992]. Solution sampler data were used for the mean breakthrough curve at each depth.

The soil water content data from each of the subplots were treated as independent values coming from a homogeneous population. This implies that the soil water content field is considered stationary in the horizontal (x - y) directions. However, nonstationarity in the vertical (z) direction and in time were accounted for. The areal mean water content in the experimental field at depth z_j and time t was estimated as

$$\langle \theta(z_j, t) \rangle = \frac{1}{N} \sum_{i=1}^N \theta_i(z_j, t) \quad (27)$$

where $\theta_i(z_j, t)$ is the water content observed on the i th subplot at depth z_j and time t , and N denotes the number of subplots in the experimental field site. Figure 3 shows the areal mean soil water content as a function of soil depth during steady state. From Figure 3 the nonstationarity (statistical nonuniformity) in the soil water content with respect to soil depth can be seen clearly. Similarly, the variance and spatial covariance of soil water content in the experimental field were estimated as

$$\text{Var} [\theta(z_j, t)] = \frac{1}{N} \sum_{i=1}^N [\theta_i(z_j, t) - \langle \theta(z_j, t) \rangle]^2 \quad (28a)$$

$$\text{Cov} [\theta(z_j, t), \theta(z_j - \xi_k, t)] = \frac{1}{N} \sum_{i=1}^N [\theta_i(z_j, t) - \langle \theta(z_j, t) \rangle] \cdot [\theta_i(z_j - \xi_k, t) - \langle \theta(z_j - \xi_k, t) \rangle] \quad (28b)$$

where $\xi_k (= z_j - z_k)$ is a dummy variable denoting separation distance between two soil depths, z_j and z_k .

The spatial covariance function of soil water content with positive separation distance ξ needs to be interpolated in order to calculate $b(z, t)$ in (15). The integral for $b(z, t)$ requires

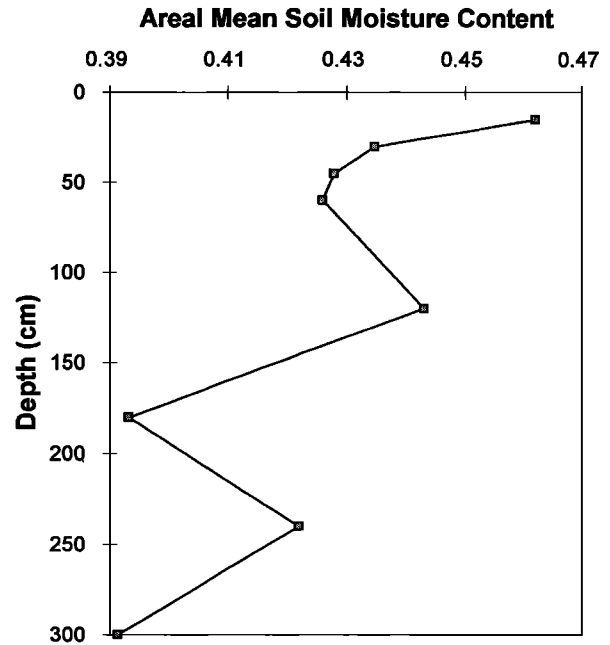


Figure 3. Areal mean soil water content estimated from field data during steady state flow.

the covariance function to be defined at all locations for the separation distance ξ within the depth interval $(0, z)$, and the covariance function can be estimated only for a limited number of ξ points from the experimental data. Generally, the spatial covariance of soil water content decreases with increasing spatial separation. Figure 4 shows the spatial covariance function of soil water content from the field data for various soil depths z as a function of separation distance ξ .

Function $b(z, t)$ in (15) for soil depth $z (= z_j)$ and time t is estimated by the formula

$$b(z_j, t) = \int_0^{z_j} d\xi \text{Cov} [\theta(z_j, t), \theta(z_j - \xi, t)]$$

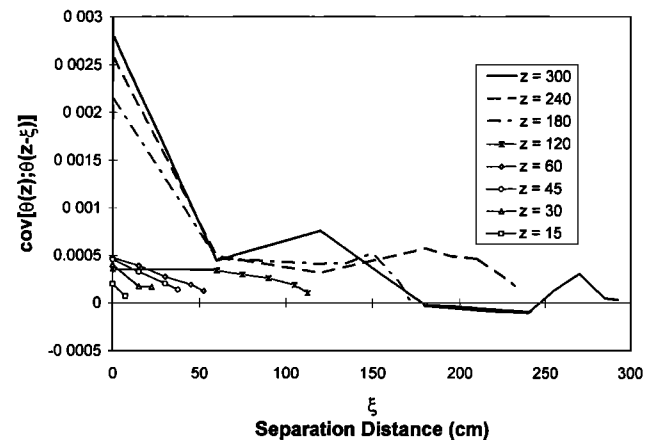


Figure 4. Covariance function of soil water content estimated from the field data as a function of separation distance at various soil depths.

Table 1. Soil Water Parameters Estimated From Field-Observed Soil Water Content

z , cm	$\langle \theta \rangle$	Var (θ)	$B(z)$	$G(z)$	$R(z)$
15	0.462	1.99E-04	0.021	7.53	36.0
30	0.435	4.03E-04	0.101	14.26	31.7
45	0.428	4.57E-04	0.273	20.73	28.0
60	0.426	4.75E-04	0.527	27.13	26.4
120	0.443	3.59E-04	2.23	53.20	25.2
180	0.393	2.15E-03	8.72	78.20	18.7
240	0.422	2.58E-03	20.98	102.75	15.9
300	0.391	2.80E-03	35.20	127.14	15.2

Read 1.99E-04 as 1.99×10^{-4} .

$$= \sum_{k=1}^J (\xi_k - \xi_{k-1}) \text{Cov} [\theta(z_j, t), \theta(z_j - \xi_k, t)] \quad (29)$$

where the estimates (equation (28b)) for the $\text{Cov} [\theta(z_j, t), \theta(z_j - \xi_k, t)]$ are utilized in (29). Finally, the parameters $G(z, t)$ and $B(z, t)$ at depth z_j and time t are estimated as

$$G(z_j, t) = \sum_{i=1}^J \langle \theta(z_i, t) \rangle (z_i - z_{i-1}) \quad (30a)$$

$$B(z_j, t) = \sum_{i=1}^J (z_i - z_{i-1}) b(z_i, t) \quad (30b)$$

As may be seen from mathematical conditions (17) and (18) for the goodness of the approximate solution (16a), the value of the ratio

$$R(z, t) = \frac{G(z, t)}{\sqrt{2B(z, t)}} \quad (31)$$

determines how good an approximation the solution (16a) is to the true pdf of $\Phi(z, t)$. Table 1 shows the observed areal mean soil water content, the observed areal variance of soil water content, and the estimated values of B , G and R at the eight observation depths under steady state flow. It is seen that for all values of soil depth z , the ratio $R(z, t)$ is greater than the value of 4, which corresponds to an error of 0.00001 probability mass. Therefore, for the limited field data, corresponding to the above described drainage experiment at the University of California, Davis, field site, the approximate solution (16a) is an almost exact solution to the Fokker-Planck PDE system (14a), (14b), (14c), and (14d') for the pdf of the soil water storage volume $\Phi(z, t)$. Therefore on the basis of the field data, expression (16a) and, consequently, expressions (19) and (20), are accepted as theoretical representations of the pdf of soil water storage volume and the ensemble CDF and pdf of solute travel time, respectively. However, the performance of the probability distributions of solute travel time will be studied below with respect to field observations.

For steady state flow conditions, $q(0, t) = q_s$, the parameters $G(z, t)$ and $B(z, t)$ become $G(z)$ and $B(z)$. Although it is constant with respect to time, the water flux $q(0, t)$ at soil surface is spatially heterogeneous in this experiment and can be viewed as a random variable. The theoretical pdf of solute travel time at depth z , conditional on surface water flux q_s , can be expressed as

$$g_{T(z)}(t|q_s) = f_{T(z)}(t|q_s t) \\ = \frac{q_s}{\sqrt{4\pi B(z)}} \exp \left[-\frac{1}{2} \frac{[q_s t - G(z)]^2}{2B(z)} \right] \quad (32)$$

The theoretical pdf of solute travel time for the experimental field can then be expressed by

$$f_{T(z)}(t) = \int g_{T(z)}(t|q_s) f_q(q_s) dq_s \quad (33)$$

where $f_q(q_s)$ is the pdf of q_s .

When N sample measurements of surface water flux q_s , $\{q_s(k), k = 1, N\}$, are available over the experimental field, the theoretical pdf of solute travel time at depth z_j can be estimated by

$$\hat{f}_{T(z_j)}(t) \equiv \sum_{k=1}^N \frac{q_s(k)}{\sqrt{4\pi B(z_j)}} \exp \left[-\frac{1}{2} \frac{[q_s(k)t - G(z_j)]^2}{2B(z_j)} \right] \\ \cdot \hat{f}(q_s(k)) [q_s(k) - q_s(k-1)] \quad (34)$$

where $q_s(k)$ is the k th sample measurement of the random steady surface water flux q_s , $\hat{f}_{T(z_j)}(t)$ is the estimator of solute travel time pdf, and $\hat{f}(q_s(k))$ is the sample relative frequency histogram of steady soil surface water flux throughout the experimental site, obtained from field data. Here the observed sample of q_s values, $q_s(k), k = 1, \dots, N$, are ordered so that $q_s(1) \leq q_s(2) \leq \dots \leq q_s(k-1) \leq q_s(k) \leq \dots \leq q_s(N)$, and $q_s(0) = 0$. Also, $t = 0$ corresponds to the beginning of the chloride application.

Figure 5 shows the theoretical probability density functions of solute travel times, as computed by (34), to soil depths of (top to bottom) 15, 30, and 45 cm, under steady and areally heterogeneous surface water flux (sample relative frequency histogram of surface water flux, obtained from field data, is shown in Figure 2). The corresponding sample relative frequency histograms from the TDR observations are also included in these figures. For the 15 cm depth the theory predicts a much more peaked pdf compared with the corresponding sample relative frequency histogram, although the peak locations are at the same travel time. One possible reason for this is that at 15 cm depth, which is quite close to the surface, the theory seems to give considerable weight to the influence of the random behavior of surface water flux on the solute travel time pdf. The peakedness of the sample relative frequency histogram of surface water flux, as seen in Figure 2, is translated into the solute travel time pdf at this depth. Another possible reason is that the near-surface water content is larger than measured at the 15 cm depth by the neutron probe. An underestimation of θ would underestimate the variance of the solute travel time pdf (through expressions (29) and (30b)) at 15 cm depth. This would result in the observed behavior of the estimated theoretical pdf (through expression (34)) at 15 cm depth. The observed pdf is not entirely smooth due to the averaging of data from more than 100 TDR locations with very different arrival times. The comparisons of theoretical and observed results at 30 and 45 cm show good agreements. This suggests that the analytical solution for solute travel time probability densities can be utilized for soil depths which are greater than or equal to 30 cm, in estimating the chance of a particular conservative pollutant reaching beyond some pre-specified soil depth.

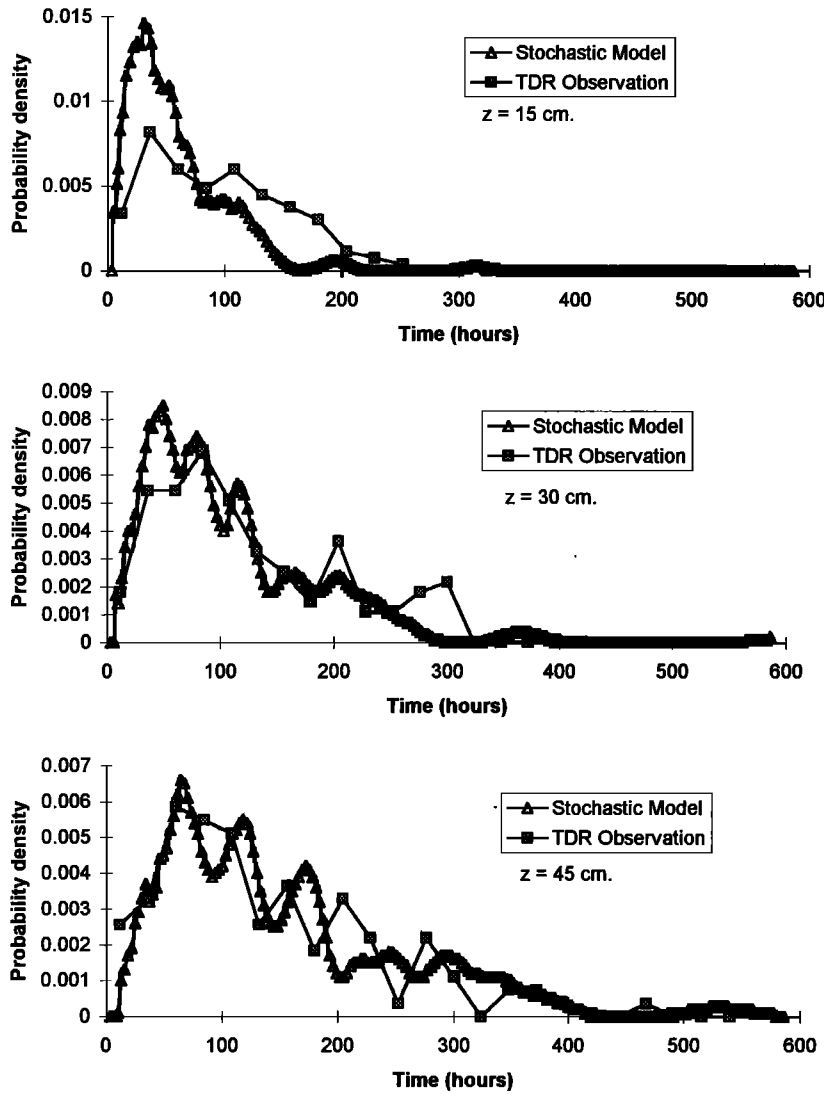


Figure 5. Comparisons of the theoretical probability density function of solute travel time and the corresponding sample relative frequency histogram from time domain reflectometry observations at soil depths $z = 15, 30$, and 45 cm.

Next, the theoretical expression (26) will be compared against areal mean chloride concentrations as they change with soil depth z and time t . Here it may be noted that although chloride transport takes place with steady water flow within the soil, the surface chloride loading (the upper boundary condition for chloride transport) is a rectangular pulse with finite time duration. Therefore mean chloride concentration will vary not only with respect to soil depth but also with respect to time. In other words, the chloride transport is a nonstationary process both in time and with respect to soil depth. Since (26) is based fundamentally upon the CDF of solute travel times, these comparisons of $\langle C(z, t) \rangle$ with field observations will constitute an indirect test of the validity of (21) as a model for the CDF of solute travel times, especially at depths which are below the 45-cm range of TDR measurements.

Using expression (26), the theoretical mean solute concentration over a field plot is estimated by

$$\langle \widehat{C}(z, t) \rangle = c_0 \left[\int_0^t \int_{t-t_0}^t \hat{f}_{T(z)}(\tau) d\tau \right] \hat{f}(t_0) dt_0$$

$$+ c_0 \left[\int_0^t \hat{f}_{T(z)}(\tau) d\tau \right] \hat{P}(t_0 \geq t) \quad (35)$$

where $\hat{f}_{T(z)}(t)$ is expressed by (34), $\hat{f}(t_0)$ is the sample relative frequency histogram, and $\hat{P}(t_0 < t)$ is the sample CDF of the random solute pulse duration t_0 . In (35) the sample probability $\hat{P}(t_0 \geq t)$ is calculated by $[1 - \hat{P}(t_0 < t)]$. Also, in (35), all the integrals are calculated numerically. The theoretical mean solute (chloride) concentrations as functions of soil depth and time, as estimated by (35), are compared against the corresponding areal mean solute (chloride) concentrations, obtained from the field experimental data, in Figure 6 for soil depths of 30, 60, and 120 cm, and Figure 7 for 180, 240, and 300 cm. From these figures it can be seen that the theoretical predictions of the mean solute concentration are acceptable at all depths except at 30 cm. Chloride mass balances range from a little more than 100% at the 30 and 60 cm depths, around 100% at 120 and 180 cm depths, and 80% at the 240 and 300 cm depths. The lack of complete recovery at the deeper depths

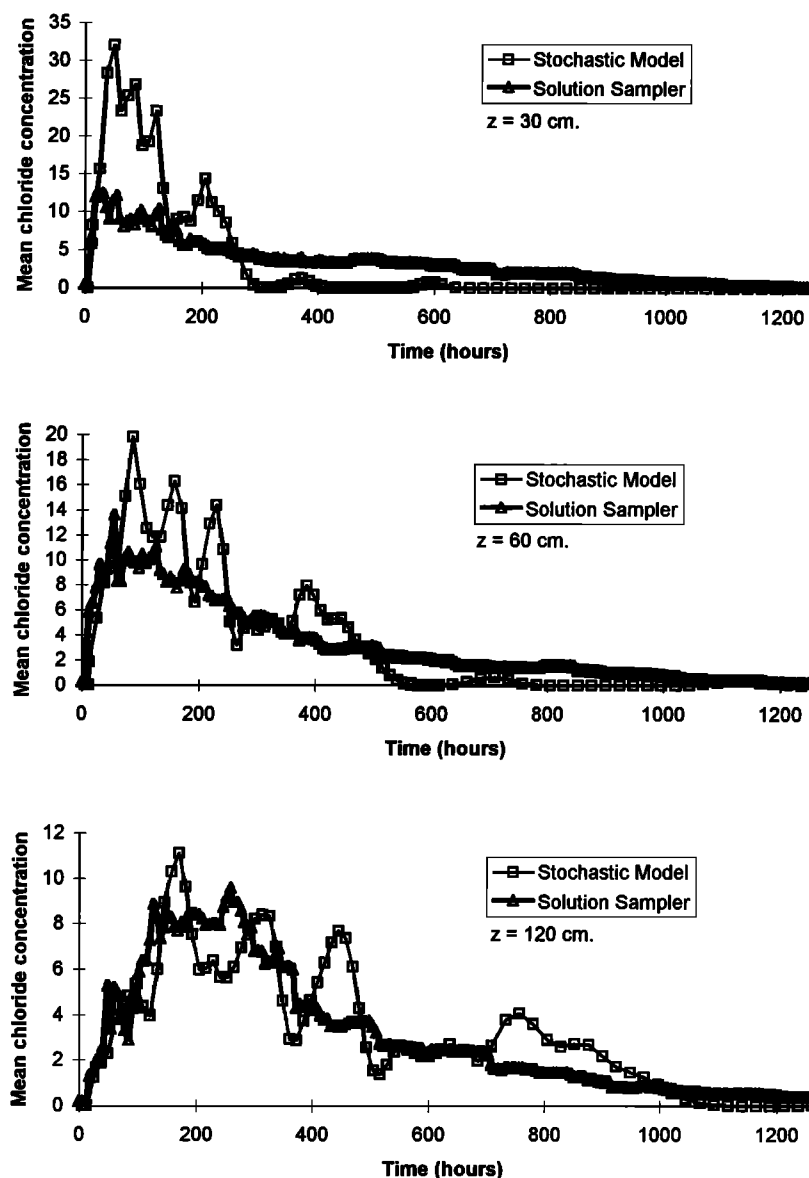


Figure 6. Comparisons of the theoretical mean solute (chloride) concentration (meq per liter) at field scale, obtained from the stochastic model (stochastic model), and the areal mean solute (chloride) concentration, obtained from the field experiment (solution sampler) at soil depths $z = 30, 60$, and 120 cm.

is likely due to some chloride still leaching past those depths at the time the experiment was terminated. The discrepancy between theory and observation at 30 cm appears to be due to an unexplained problem with the experimental observation for this depth. Although solute mass recovery is slightly more than 100% for this depth, the peak height is smaller than that of the 60 cm depth. This is inconsistent with theory and with behavior of the other depths. The intensity of sampling may not have been sufficient to detect all the chloride peaks within the first few days of the experiment. One may also raise the question as to why the solute travel time comparison between the theory and the TDR observations is good at 30 cm (Figure 5), while the mean solute concentration comparison between the theory and solution sampler observations is quite bad. We hypothesize that one reason for this discrepancy is the difference in the observations of solute travel time and of solute concentration. The TDR which is used in observing the solute travel time

obtains a depth-averaged observation from the soil surface to any particular depth at any given field location. Also, there were four TDRs at each of the 24 field subplots at every computational depth. Solution samplers tend to measure solute in macropores and not necessarily the entire soil matrix. Therefore it is believed that the difference between the observational capabilities of TDRs and of solution samplers may have caused the above mentioned discrepancy.

When Figures 5, 6, and 7 are studied, one can detect oscillations in the theoretical predictions of chloride travel time pdf and mean chloride concentrations at all depths. These oscillations, which may be interpreted as multimodal theoretical pdfs in the case of solute travel time pdfs, are actually an artifact. The basic reason for these oscillations is the sampling errors which result from the direct use of the sample relative frequency histogram of surface water flux (Figure 2) in all of the predictions by means of expressions (34) and (35). As seen

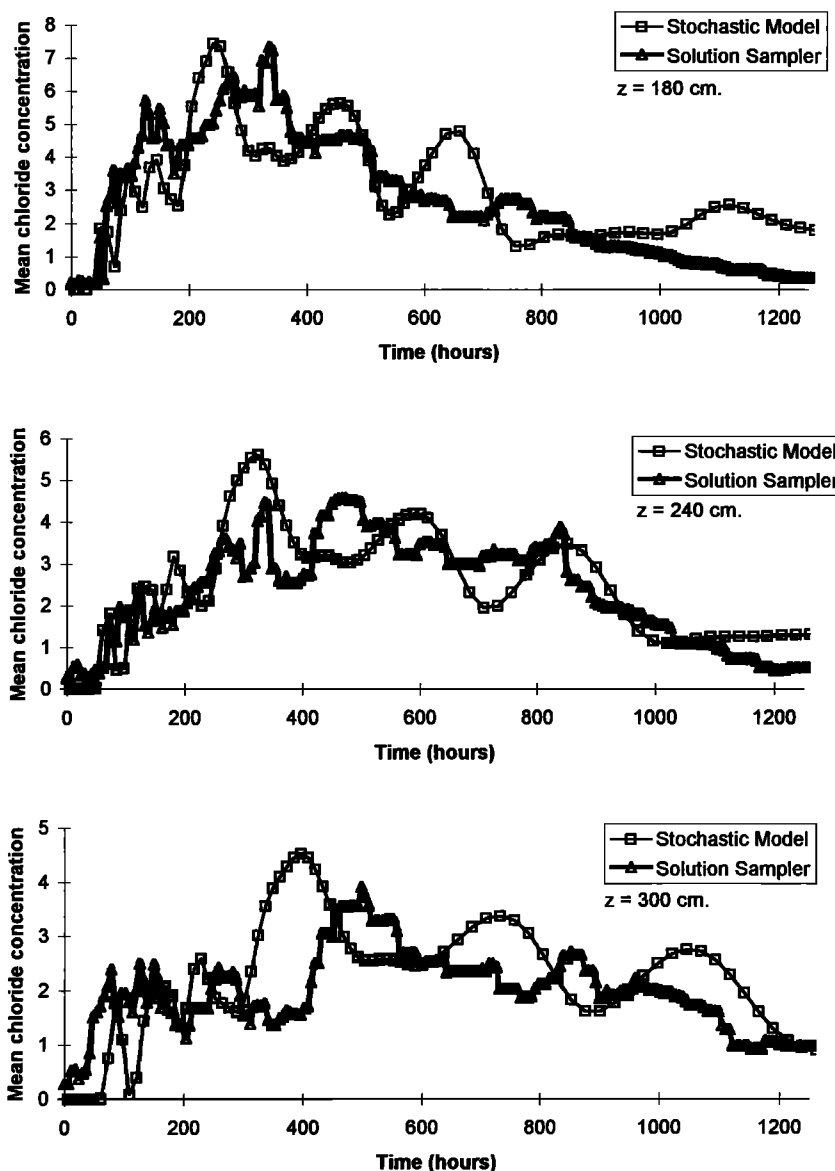


Figure 7. Comparison of the theoretical mean solute (chloride) concentration (meq per liter) at field scale, obtained from the stochastic model (stochastic model), and the areal mean solute (chloride) concentration, obtained from the field experiment (solution sampler) at soil depths $z = 180$, 240 , and 300 cm.

from Figure 2, the relative frequency histogram of surface water flux is not a smooth curve and has several void flux intervals. This histogram is actually the estimate of the surface water flux pdf which, fundamentally, is a continuous curve. However, since this continuous pdf is not known at this time, it was estimated from the field experimental data. When a continuous pdf is statistically inferred at some discrete intervals, some fluctuation of the estimates occurs due to having a finite-size sample from the experimental data. When one uses the sample relative frequency histogram values $\hat{f}(q_s(k))$, $k = 1, \dots, N$ in expression (34), one can see from this expression that the fluctuations in the $\hat{f}(q_s(k))$ values translate into oscillations in the solute travel time pdf theoretical estimates $\hat{f}_{T(z)}(t)$ which are seen in Figure 5. In turn, when one uses these solute travel time pdf estimates in expression (35) for the theoretical estimates of mean solute concentration $\langle C(z, t) \rangle$, the oscillations in the estimates $\hat{f}_{T(z)}(t)$ result in

the oscillations in $\langle C(z, t) \rangle$, as seen in Figures 6 and 7. However, in order to stay as close as possible to the observed soil water flow behavior, the relative frequency histogram of surface water flux was not smoothed in the theoretical computations.

As seen in Figures 3 and 4, the areal mean water content and water content covariance estimates are also not smooth curves. However, in the theoretical computations in (34) and (35), only the integrals $G(z)$ and $B(z)$, for the mean and covariance of the water content, respectively, are used. Since integration is a smoothing operation, the fluctuations in the field estimates of the mean and covariance of the water content are smoothed out by these integration operations and do not cause significant fluctuation in the theoretical estimations of the solute travel time pdf and mean solute concentration.

It is also interesting to note from Figures 6 and 7 that the observed mean chloride concentration curves also oscillate

below 180 cm. A possible explanation for these oscillations is the observed layering of the University of California, Davis, field soil at around 180 cm (as may be seen from Figure 3 for the areal mean water content profile and from Figure 4 for water content covariance). The authors believe that owing to soil layering, the solute breakthrough curve below 180 cm shows a multiple number of peaks. Furthermore, the literature has examples where field-averaged concentration profiles can have multiple peaks [Amoozegar-Fard *et al.*, 1982].

Summary and Conclusions

This study addressed the development of probability distribution functions of travel times for stochastic time-depth nonstationary (but horizontally stationary) field-scale, vertical convective conservative solute transport. The time-depth evolutionary probability distribution functions of solute travel times were developed directly from the convective solute transport equation under unsteady and nonuniform soil water flows with their corresponding initial conditions (ICs) and upper boundary conditions (UBCs). At the beginning of the theoretical development, time-varying solute concentration UBCs and depth-varying solute concentration ICs were also considered. However, as shown above, in the derivation of the probability distributions of solute travel times, only the depth-varying ICs and time-varying UBCs of soil water flows need to be considered. Utilizing the analytical continuum solution from the convective transport equation for the solute front, the time–soil depth evolving theoretical cumulative distribution function (CDF) and theoretical probability density function (pdf) of conservative solute travel times were obtained. The soil surface water flux (infiltration rate), although considered generally as time varying in the solutions, was first considered as deterministic. Then the theoretical time–soil depth evolving CDF of solute travel times was generalized to the case of both stochastic porous media and stochastic surface water flux (infiltration). Finally, the theoretical mean solute concentration, as a function of soil depth and time, was developed by means of the CDF of solute travel times under the rectangular pulse solute loading upper boundary condition. This condition corresponds to the performed field experiment on chloride transport at the University of California, Davis, experimental station.

Although the theoretical derivation for the probability distributions of conservative solute travel time were started from the point-scale (individual soil column scale) convective transport equation, dispersion emerged naturally in the ensemble CDF and ensemble pdf of solute travel times due to the stochasticity of the soil water content, as seen from (16b), (19), (20), and (21). The dispersion phenomenon can also be seen from the Fokker-Planck equation (14a) for the pdf of soil water storage volume. The dispersion is defined in terms of the spatial integral of nonstationary spatial covariance (varies with soil depth) of the soil water content random field with respect to the depth separation distance. In general, this covariance also changes with time t , and thereby reflects the nonstationary, transient behavior of the soil water content random field. The time–soil depth nonstationarity of the soil water content random field is incorporated into the ensemble CDF and pdf of solute travel times also through the time–soil depth varying mean soil water content, as may be seen from (16c), (19), (20), and (21).

At this point, it is important to note that the pdf of soil water storage volume, as seen in expression (16a), has as its param-

eters the mean $\langle \theta(z, t) \rangle$ and covariance $\text{Cov}[\theta(z, t); \theta(z - \xi, t)]$ of soil water content over a field. In turn, the CDF of solute travel times, as seen in expression (21), also depends on the mean and covariance functions of soil water content over a field. As such, a complete solution for the probability distribution of solute travel times necessitates the development of the theoretical expressions for the mean and covariance functions of soil water content at field scale. Such a development requires very substantial theoretical work on the soil water flow dynamics under unsteady and nonuniform flow conditions, in general, and was not pursued in this study. Instead, the mean and covariance functions of soil water content were estimated from field experimental data.

As may be seen from (20), the probability distribution for the conservative solute travel times is not Gaussian, even in the case of deterministic surface water flux. This is due to the time variation in the surface water flux.

As was mentioned in several places during the theoretical development, the derived theoretical CDF and pdf of conservative solute travel times are approximate. This approximation is to the order of the covariance of the soil water content random field ($z_c \text{Var}[\theta(z, t)]$). It also depends on the value of $R(z, t)$, as defined by a ratio between $G(z, t)$ and the square root of twice $B(z, t)$. The limited field data, as obtained from a steady state flow drainage experiment at the University of California, Davis, field site, indicates the plausibility of the approximate solutions.

In order to explore the validity of the derived ensemble CDF and pdf of solute travel times further, the performance of the probability distributions of solute travel time were studied with respect to field observations. The comparison of theoretical pdfs and corresponding relative frequency histograms of solute travel times shows good agreement at soil depths of 30 and 45 cm, while the agreement is not good at the shallow depth of 15 cm (Figure 5). This suggests that the analytical solution for solute travel time probability densities can be utilized for soil depths which exceed 30 cm, in estimating the chance of a particular conservative pollutant reaching beyond some pre-specified soil depth, provided that the mean and covariance functions of soil water content are known.

Also, as an indirect test of the theoretical CDF of solute travel times, the theoretical mean solute concentrations (which depend fundamentally on the CDF of solute travel times), corresponding to rectangular pulse solute loading upper boundary conditions, were compared against corresponding mean areal solute concentrations, estimated from field experimental data on chloride transport. As seen from Figures 6 and 7 for soil depths of 30, 60, 120, 180, 240, and 300 cm, the theoretical predictions of the mean solute concentration are quite acceptable at all depths except 30 cm. Here it may be noted that in the field experiment, although chloride transport takes place with steady and nonuniform water flow within the soil, the surface chloride loading (the upper boundary condition for chloride transport) is a rectangular pulse with finite time duration. Therefore mean chloride concentration will vary not only with respect to soil depth but also with respect to time. In other words, the chloride transport, as observed in the University of California, Davis, field experiment, is a nonstationary process both in time and with respect to soil depth.

In conclusion, from the limited experimental results presented in this study, it may be inferred that once the mean and covariance functions of the soil water content and the probability distribution of surface water flux are known over a field-

scale soil, then for one-dimensional transport and for depths exceeding 30 cm, it is possible to calculate the probability distribution of solute travel times as a function of soil depth and time by means of (21).

In order to validate firmly the theoretical solutions for the CDF and pdf of conservative solute travel times derived in this study, additional water flow and solute transport field experiments need to be conducted over field plots with different soil textures and under transient soil water flow conditions.

Appendix

Combining (10) with (13a), one obtains the operator differential equation for the evolution of the pdf of Φ , $P(\Phi; z, t)$ as follows:

$$\begin{aligned} \frac{\partial P(\Phi; z, t)}{\partial z} = & A_0(t, z) P(\Phi; z, t) + \alpha^2 \int_0^z d\xi \\ & \cdot \left\langle \left\langle \left\langle A_1(t, z) \exp \left(\int_{z-\xi}^z A_0(t, s) ds \right) A_1(t, z - \xi) \right\rangle \right\rangle \right\rangle \\ & \cdot \exp \left(- \int_{z-\xi}^z A_0(t, s) ds \right) P(\Phi; z, t) \end{aligned} \quad (A1)$$

to order $\alpha^2 z_c$. Substituting the expressions (11a) and (11b) for the operators A_0 and A_1 into (A1) yields

$$\begin{aligned} \frac{\partial P(\Phi; z, t)}{\partial z} = & -\langle \theta(z, t) \rangle \frac{\partial P(\Phi; z, t)}{\partial \Phi} \\ & + \int_0^z d\xi \left\langle \left\langle \left\langle [-\theta(z, t) + \langle \theta(z, t) \rangle] \frac{\partial}{\partial \Phi} \right. \right. \right. \\ & \cdot \exp \left(- \int_{z-\xi}^z ds \langle \theta(s, t) \rangle \frac{\partial}{\partial \Phi} \right) \\ & \cdot [-\theta(z - \xi, t) + \langle \theta(z - \xi, t) \rangle] \frac{\partial}{\partial \Phi} \left. \right\rangle \left. \right. \left. \right\rangle \\ & \cdot \exp \left(\int_{z-\xi}^z ds \langle \theta(s, t) \rangle \frac{\partial}{\partial \Phi} \right) P(\Phi; z, t) \end{aligned} \quad (A2)$$

Noting that the operators A_0 and A_1 are not functions of Φ , and also utilizing the inverse relationship (13c) reduces (A2) to

$$\begin{aligned} \frac{\partial P(\Phi; z, t)}{\partial z} = & -\langle \theta(z, t) \rangle \frac{\partial P(\Phi; z, t)}{\partial \Phi} \\ & + \int_0^z d\xi \left\langle \left\langle \left\langle [-\theta(z, t) + \langle \theta(z, t) \rangle] \right. \right. \right. \\ & \cdot [-\theta(z - \xi, t) + \langle \theta(z - \xi, t) \rangle] \left. \right\rangle \left. \right. \left. \right\rangle \frac{\partial^2 P(\Phi; z, t)}{\partial \Phi^2} \end{aligned} \quad (A3)$$

to order $\alpha^2 z_c$. Then noting (equation (13d)) that $\langle \langle \langle \rangle \rangle \rangle$ is a covariance operator yields the expression (14a).

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