Title

Solution Methodology and Validation of Physics-based Stochastic Subsurface Solute Transport Equations

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ABSTRACT

This research project addresses the quantification of the risks due to contaminant (solute) concentrations in field-scale soils as contaminants migrate under various pollution loadings at the soil surface (boundary conditions), starting with initial contaminant plumes existing within the soil medium prior to the beginning of loadings (initial conditions). 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 statistical heterogeneity of the soil profile. For the quantification of soil contamination risks, first, almost exact ensemble probability distribution functions of solute travel time for stochastic vertical convective solute transport within above-described heterogeneous field scale soils under both deterministic and stochastic water application rates and unsteady-nonuniform moisture flows were derived directly from the convective transport stochastic partial differential equation (PDE) under general depth-varying initial and time-varying boundary conditions. Secondly, almost exact ensemble pdfs of solute concentrations as function of time and soil depth for stochastic vertical convective solute transport within above-described field-scale, heterogeneous soils under both deterministic and stochastic water application rates were derived directly from the convective transport stochastic PDE under various depth-varying initial and time-varying boundary conditions. Field data from the water and solute transport experiments at U.C. Davis field site showed that the approximation, used in the above ensemble pdfs, is exact for the particular field site. The derived ensemble pdfs for solute concentrations were verified by Monte Carlo simulation solutions of the convective transport stochastic PDE. The derived ensemble pdfs unify the Eulerian and Lagrangian components of transport in one single framework since they contain explicitly the influence of both initial and boundary conditions. They also show that the derived pdfs for both solute travel times and solute concentrations are non-Gaussian under the influence of initial and boundary conditions.

analyzed the evolution of the field scale breakthrough curve as function of depth in terms of the first two moments of solute travel time.

Although the above-mentioned studies have established the fundamental stochastic convective nature of solute transport at field-scale soils, it was Russo (1991) who established the essentially one-dimensional, vertical nature of this transport, and the importance of vertical soil heterogeneity (this issue was also stressed in the experimental study of Butters and Jury, 1989) and the importance of transient flow conditions 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. 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 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 "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 project addresses the problem on the development of ensemble pdfs of stochastic time-depth nonstationary (but horizontally stationary) field-scale, vertical convective solute transport. The development of the time-depth evolutionary pdfs of solute concentrations and solute travel times are obtained directly from the convective solute transport equation under general unsteady and nonuniform soil moisture flows and under time-varying solute concentration UBCs and depth-varying solute concentration ICs. First, the pathwise deterministic analytical continuum solution of vertical convective solute transport is obtained. In order to verify this solution, it is combined with a Green-Ampt analytical solution of vertical soil moisture flows and tested against the numerical solution of convective solute transport equation combined with the numerical solution of vertical Richard's equation. Secondly, utilizing the analytical continuum solution of convective transport equation, the general ensemble pdf of solute travel time is obtained. Then the time-depth dependent ensemble pdf of solute concentration is developed under general initial and boundary conditions. It is shown that this solution combines the popular Eulerian and Lagrangian approaches to solute transport modeling under one framework. The theoretical solute concentration pdfs are then verified by Monte Carlo solutions. The above developments consider the stochasticity in the flow and solute concentration fields due mainly to field-scale soil heterogeneity. The water application (recharge or input water flux) rates, although considered generally as time-varying in the solutions, are taken as deterministic. In the final section of this project, the water application rates are also randomized and the previous developments are generalized accordingly.

For the experimental part of this research, a field site on the UC Davis campus was intensively instrumented for the determination of soil water flow hydraulic characteristics and of solute transport characteristics for a conservative solute (potassium chloride) and a reactive solute (atrazine). These experimental results are being utilized in the validation of theoretical developments achieved by this project on field-scale solute transport.

I.2 Research Objectives

Within the framework of the above problem statement the objectives of this research project may be stated as:

a) To derive the ensemble probability density functions (pdf) of solute concentrations and solute travel times for stochastic time-depth nonstationary (but horizontally stationary) field-scale, vertical convective solute transport directly from the transport equation under general initial and boundary conditions;

b) To validate the derived ensemble pdfs by Monte Carlo solutions of convective solute transport;

c) To perform experiments at a UC Davis agricultural field for determination of soil water flow hydraulic characteristics and solute transport characteristics for a conservative and a reactive solute at field scale; to utilize the experimental results for validation of the theoretical results.

III. METHODOLOGY

The convective vertical transport equation for a conservative solute through a vertically heterogeneous soil by unsteady-nonuniform soil moisture flow is expressed as (Simmons, 1982);

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

where C denotes time-depth dependent solute concentration, z is depth coordinate (positive downwards), t is time, q is local Darcy flux in the vertical direction, and θ is the local volumetric moisture content. In (1) it is assumed that the solid phase is incompressible soil and liquid phase is incompressible, constant density fluid. We are also assuming 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 and boundary conditions for soil moisture flows are,

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

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

and the conditions for solute transport are,

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

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

Using the theory of first-order partial differential equations (PDE) (Hildebrand, 1976) the general deterministic analytical continuum solution of the vertical convective solute transport through a vadose zone is obtained as

$$C(z,t) = g\left[\int_0^z \theta(\xi,t)\, d\xi - \int_0^t q(0,\tau)\, d\tau\right] \tag{3}$$

where g[•] is a function whose form is to be determined from ICs and UBCs. To achieve an explicit analytical solution from (3) it is necessary to specialize the moisture flow IC $\theta_n(z)$ to any explicit, invertible function of z, and to specialize the moisture flow UBC $q_o(t)$ to any explicit, invertible function of t. Meanwhile, the solute transport IC $C_n(z)$ and UBC $C_o(t)$ may be left in their general form provided they are understood to be invertible functions. Consequently, we take for moisture flows,

IC: $\theta_n(z) = \theta_o$, a constant , $z > 0$ (3a)

UBC: $q_o(t) = q_o$, a constant , $t > 0$ (3b)

and for solute transport, (2c) and (2d) as IC and UBC. Then under (3a), (3b), (2c) and (2d) the general analytical continuum solution of vertical convective solute transport specializes to the explicit form

$$C(z,t) = C_n\left[\frac{1}{\theta_0}\left\{\int_0^z \theta(\xi,t)\, d\xi - q_0 t\right\}\right] \cdot U\left(\int_0^z \theta(\xi,t)\, d\xi - q_o t\right)$$

$$+C_0\left[\frac{1}{q_0}\left\{-\int_0^z \theta(\xi,t)\, d\xi + q_0 t\right\}\right] \cdot U\left(-\int_0^z \theta(\xi,t)\, d\xi + q_o t\right) \quad , z \geq 0, t \geq 0 \tag{4}$$

where the step function U(•) is defined by

$$U(\alpha) = 1 \quad \text{if} \quad \alpha > 0$$
$$0 \quad \text{if} \quad \alpha \leq 0 \tag{4a}$$

If (3a) and (3b) were generalized to a depth-dependent IC,

IC: $\theta_n(z) = \theta_o z$, $z > 0$ (3c) and time-dependent UBC,

UBC: $q_0(t) = q_o t \quad , t > 0$ (3d)

then under (2c), (2d), (3c) and (3d) the general deterministic continuum solution (3) takes the special explicit form

$$C(z,t) = C_n\left[\sqrt{\frac{2}{\theta_0}\left\{\int_0^z \theta(\xi,t)\,d\xi - q_0\frac{t^2}{2}\right\}}\right]\cdot U\left(\int_0^z \theta(\xi,t)\,d\xi - \frac{t^2}{2}q_o\right)$$

$$+ C_0\left[\sqrt{-\frac{2}{q_0}\left\{\int_0^z \theta(\xi,t)\,d\xi - \frac{t^2}{2}q_0\right\}}\right]\cdot U\left(-\int_0^z \theta(\xi,t)\,d\xi + \frac{t^2}{2}q_o\right) \quad , z \geq 0, t \geq 0 \qquad (5)$$

The explicit analytical continuum solution (4) for vertical convective solute transport under (2c), (2d), (3a) and (3b) was combined with a Green-Ampt analytical solution of vertical soil moisture flows and tested against the numerical solution of convective solute transport equation combined with the numerical solution of vertical Richard's equation with very satisfactory results.

The solute travel time cumulative probability distribution function (CDF) under the general ICs and BCs (2a), (2b), (2c) and (2d) is obtained from (3) as

$$P[T(z) < t] = P\left[\int_0^z \theta(\xi,t)\,d\xi < \int_0^t q(0,\tau)\,d\tau\right]. \qquad (6)$$

and defining $\Phi(z,t)$ by

$$\Phi(z,t) = \int_0^z \theta(\xi,t)\,d\xi \quad , \qquad (7)$$

$$P[T(z) < t] = P\left[\Phi(z,t) < \int_0^t q(0,\tau)\,d\tau\right] \quad . \qquad (6a)$$

Therefore, in order to obtain an explicit expression for the probability distribution of travel times directly from the convective transport equation (1) under (2a), (2b), (2c) and (2d) it is necessary to derive the pdf of the cumulative water in the soil profile from surface to a depth z at time t.

Using the phase space-cumulant expansion methodology as described in Kavvas and Govindaraju (1991), the Fokker-Planck system for the pdf of $\Phi(z,t)$, $P(\Phi, z,t)$ is obtained as

$$\frac{\partial P(\Phi, z,t)}{\partial z} = -\langle\theta(z,t)\rangle \frac{\partial P(\Phi, z,t)}{\partial \Phi}$$

$$+ \int_0^\infty d\xi \, \mathrm{Cov}\left[\theta(z,t); \theta(z-\xi,t)\right] \cdot \frac{\partial^2 P(\Phi, z,t)}{\partial \Phi^2} \qquad (8a)$$

IC: $P(\Phi, 0, t) = \delta_+(\Phi)$

UBC: $$-\langle\theta(z,t)\rangle P(\Phi,z,t) + \int_0^\infty d\xi \, \mathrm{Cov}\left[\theta(z,t); \theta(z-\xi,t)\right] \cdot \frac{\partial P(0, z,t)}{\partial \Phi} = 0$$

Compatibility: $$\int_0^\infty P(\Phi,z,t)\, d\Phi = 1 \qquad (8b)$$

for soil depths $z > z_c$ and to order z_c Var[$\theta(z,t)$] where z_c is the correlation length of $\theta(z,t)$. One can notice from (8a) that for the ensemble pdf of $\Phi(z,t)$ (and, thereby, of solute travel times) at field-scale, the dispersion appears naturally in the Fokker-Planck equation for $P(\Phi,z,t)$ due to field heterogeneity as manifested by the spatial covariance of the soil moisture content. The Fokker-Planck system (8a) and (8b) has no known explicit analytical solution. However, the following approximate analytical solution was developed;

$$P(\Phi,z,t) = \frac{1}{\sqrt{4\pi B(z,t)}} \exp\left\{-\frac{1}{2}\left[\Phi - H(z,t)\right]^2 / 2B(z,t)\right\} \quad , z \geq 0; \Phi \geq 0 \qquad (9a)$$

where $$B(z,t) = \int_0^z du \int_0^\infty d\xi \, \mathrm{Cov}\left[\theta(u,t); \theta(u-\xi,t)\right], \qquad (9b)$$

$$H(z,t) = \int_0^z < \theta(\xi,t) > d\xi \qquad (9c)$$

It may be noted from (9) that the pdf of $\Phi(z,t)$ varies with time t and depth z. It was also possible to derive an explicit mathematical condition for the validity of the approximate analytical solution (9). For

$$H(z,t) > [32B(z,t)]^{1/2} \tag{10a}$$

the approximate analytical solution (9) satisfies the Fokker-Planck system (8) with 99.9999% precision while for

$$H(z,t) > 2.33\,[2B(z,t)]^{1/2} \tag{10b}$$

the approximate solution (9) satisfies (8) with 99% precision. Therefore, for all practical purposes once the soil moisture flow stochastic process satisfies the less stringent condition (10b), the approximate solution (9) becomes an almost exact solution to the system (8) for the pdf of $\Phi(z,t)$. It may be noted from (9) that the approximate solution (9) for the pdf of $\Phi(z,t)$ is Gaussian with mean $H(z,t)$ and variance $B(z,t)$.

Combining (9) with (6) one obtains the almost exact CDF of solute travel times directly from the vertical convective solute transport equation under the general moisture and concentration initial and boundary conditions (2a), (2b), (2c) and (2d), as

$$P\left[T(z) < t \,\middle|\, \int_0^t q(0,\tau)d\tau\right] = F_\Phi\left(\int_0^t q(0,\tau)\,d\tau\right) = S\left(\frac{\int_0^t q(0,\tau)\,d\tau - \int_0^z <\theta(\xi,t)> d\xi}{\sqrt{2\int_0^z du \int_0^\infty d\xi \,\mathrm{Cov}\,[\theta(u,t);\, \theta(u-\xi,t)]}}\right) \tag{11}$$

where F_Φ denotes the CDF of $\Phi(z,t)$ while $S(\cdot)$ is the CDF of a Standard Gaussian (Normal) random variable. Expression (11) shows clearly that solute travel time CDF depends upon the input moisture flux (water application rate) $q(0,\tau)$ at soil surface and on the mean and covariance behavior of the soil moisture content stochastic function at field scale. It may be pointed out that in (11) $q(0,\tau)$ is deterministic. Its randomization shall be dealt with later. Although, the CDF of solute travel time looks as if Gaussian, it actually is not. The pdf of solute travel time, $f_{T(z)}(t)$, is obtained from (11) as

$$f_{T(z)}\left(t \,\middle|\, \int_0^t q(0,\tau)d\tau\right) = dF_{\Phi}\left(\int_0^t q(0,\tau)d\tau\right) / dt$$
$$= P\left(\int_0^t q(0,\tau)d\tau, z, t\right) \cdot q(0,t) \qquad (12)$$

Hence, from (12) it follows that although the pdf $P(\Phi,z,t)$ of $\Phi(z,t)$ is almost Gaussian, as long as the water application rate $q(0,t)$ at soil surface varies with time t, the pdf of the solute travel time will be non-Gaussian.

Next we obtain the time-depth dependent ensemble pdf of solute concentration under both ICs and UBCs of vertical soil moisture flows and solute concentrations at field-scale. In this derivation we initially consider the stochasticity only due to soil heterogeneity which is considered nonstationary with respect to soil depth (vertical soil statistical heterogeneity) but stationary in the horizontal plane. The solute concentration process will, however, be time-depth nonstationary due to the time-depth varying solute concentration initial and boundary conditions even if the soil moisture flows were taken steady and uniform. Hence, the vertical convective solute transport equation (1) becomes a stochastic partial differential equation (SPDE) when it is viewed as a model of vertical solute transport at field scale. The concentration pdf shall be obtained directly from (1).

The analytical solution (4) to the vertical convective solute transport equation under the ICs and UBCs (2c), (2d), (3a) and (3b) is a pathwise solution when the transport equation (1) is considered as a SPDE under the stochasticity of soil moisture flows due to field-scale soil heterogeneity. In general, the pdf of time-depth varying solute concentration, for given deterministic water application rates $q(0,t)$, follows from the general pathwise solution (3) to the stochastic convective solute transport equation (1) as follows,

$$f_c\left(c,z,t \,\middle|\, \int_0^t q(o,\tau)d\tau\right) = f_c\left(c \,\middle|\, \Phi \le \int_0^t q(o,\tau)d\tau\right) \cdot F_{\Phi}\left(\int_0^t q(o,\tau)d\tau\right)$$
$$+ f_c\left(c \,\middle|\, \Phi > \int_0^t q(o,\tau)d\tau\right) \cdot \left[1 - F_{\Phi}\left(\int_0^t q(o,\tau)d\tau\right)\right] \qquad (13)$$

specializing the solution to the solute transport system (1), (2c), (2d), (3a) and (3b), and utilizing the pathwise solution (4) and the almost exact pdf (9) for $\Phi(z,t)$, we obtain the time-depth evolutionary pdf of solute concentration $C(z,t)$, for given deterministic water application rates, as

$$
\begin{aligned}
f_c(c,z,t\,|\,q_o) = \sum_{\ell=1}^{J} \frac{1}{\sqrt{4\pi B(z,t)}} \exp\left\{-\frac{1}{4B(z,t)}\right\}\left[-q_o\, C_{o\ell}^{-1}(c) + q_o t - H(z,t)\right]^2 \bullet \\
\bullet \left| q_o \frac{dC_{o\ell}^{-1}(c)}{dc} \right| \bullet S\left(\frac{q_o t - H(z,t)}{\sqrt{2B(z,t)}}\right) \\
+ \sum_{\ell=1}^{m} \frac{1}{\sqrt{4\pi B(z,t)}} \exp\left\{-\frac{1}{4B(z,t)}\right\} \bullet \left[\theta_o\, C_{n\ell}^{-1}(c) + q_o t - H(z,t)\right]^2 \bullet \\
\bullet \left| \theta_o \frac{dC_{n\ell}^{-1}(c)}{dc} \right| \bullet \left[1 - S\left(\frac{q_o t - H(z,t)}{\sqrt{2B(z,t)}}\right)\right]
\end{aligned}
\tag{14}
$$

for the general case when the concentration IC function $C_n(z)$ and UBC function $C_o(t)$ have respectively finite m and J numbers of inverses, and for soil depths $z > z_c$ (where z_c is the correlation length of soil moisture content $\theta(z,t)$, to order z_c $Var[\theta(z,t)]$. It is important to note that the first summation on r-h-s of (14) is the Eulerian component of solute transport which is dictated by the upper boundary conditions, while the second summation on r-h-s of (14) is the Lagrangian component which is dictated by the initial conditions. Thus, (14), and for that matter (13), provide solution frameworks to the time-depth probabilistic behavior of solute concentration in field-scale soils where both the Eulerian and Lagrangian components are incorporated. It is also important to note that in (14) both the initial and boundary conditions for soil moisture flows and solute transport are incorporated to the ensemble pdf of solute concentrations at field-scale.

We have then developed the pdfs of solute concentration under various special cases. Special Case 1 corresponds to taking initial concentration $C_n(z) = C_n$, a constant, while considering the UBC $C_o(t)$ as a step input load, $C_o(t) = C_oU(t)$ where C_o is constant, in addition to (2a) and (2b) as general IC and UBC for soil moisture flows. Under this case

$$P\left[C(z,t)=C_o \left| \int_0^t q(o,\tau)d\tau \right.\right] = S\left(\frac{\int_0^t q(o,\tau)d\tau - H(z,t)}{\sqrt{2B(z,t)}}\right)$$

$$P\left[C(z,t)=C_n \left| \int_0^t q(o,\tau)d\tau \right.\right] = 1 - S\left(\frac{\int_0^t q(o,\tau)d\tau - H(z,t)}{\sqrt{2B(z,t)}}\right) \quad (15)$$

for soil depths $z > z_c$ and to order z_c Var $[\theta(z,t)]$.

Special Case 2 corresponds to IC $C_n(z) = 0$ and pulse input load UBC $C_o(t) = m[U(t) - U(t-t_o)]$, in addition to (2a) and (2b) as general IC and UBC for soil moisture flows. For this case, for $0 \le t \le t_o$,

$$P\left[C(z,t)=m \left| \int_0^t q(o,\tau)d\tau \right|\right] = S\left(\frac{\int_0^t q(o,\tau)d\tau - H(z,t)}{\sqrt{2B(z,t)}}\right)$$

$$P\left[C(z,t)=o \left| \int_0^t q(o,\tau)d\tau \right|\right] = 1 - S\left(\frac{\int_0^t q(o,\tau)d\tau - H(z,t)}{\sqrt{2B(z,t)}}\right) \quad (16a)$$

and for $t > t_o$,

$$P\left[C(z,t)=m \left| \int_0^t q(o,\tau)d\tau \right.\right] = S\left(\frac{\int_0^t q(o,\tau)d\tau - H(z,t)}{\sqrt{2B(z,t)}}\right) \bullet \left[1 - S\left(\frac{\int_0^{t-t_o} q(o,\tau)d\tau - H(z,t-t_o)}{\sqrt{2B(z,t-t_o)}}\right)\right] \quad (16b)$$

for soil depths $z > z_c$ and to order z_c Var $[\theta(z,t)]$.

Special Case 3 corresponds to IC $C_n(z) = 0$ and impulse input load UBC $C_o(t) = m\delta_+(t)$, in addition to (2a) and (2b) as general IC and UBC for soil moisture flows. For this case

$$f_{c(z,t)}\left(c \left| \int_0^t q(o,\tau)d\tau \right.\right) = \delta(c-m)\, P\left(\int_0^t q(o,\tau)d\tau, z, t\right) + \delta(c)\, P\left(\Phi \neq \int_0^t q(o,\tau)d\tau, z, t\right) \quad (17)$$

for soil depths $z > z_c$ and to order $z_c \mathrm{Var}[\theta(z,t)]$. (17) leads to

$$\langle C(z,t)\rangle = mP\left(\int_0^t q(o,\tau)d\tau, z, t\right)$$

where in (17) and (17a) $P\left(\int_0^t q(o,\tau)d\tau, z, t\right)$ denotes pdf of Φ evaluated at $\int_0^t q(o,\tau)d\tau$ while $P\left(\Phi \neq \int_0^t q(o,\tau)d\tau, z, t\right)$ denotes the probability of the event that $\Phi \neq \left(\int_0^t q(o,\tau)d\tau\right)$.

Finally, we consider the more general case when the water application rate q(o,t) is also taken as stochastic in addition to the stochasticity due to soil heterogeneity. Define Q(t) as

$$Q(t) = \int_0^t q(o,\tau)d\tau \quad . \tag{18}$$

The solute travel time CDF under stochastic water application rates becomes

$$P[T(z) < t] = \int F_\Phi(Q(t)) \cdot f(Q(t))\, dQ(t) \tag{19}$$

where $F_\Phi(Q(t))$ is defined in (11) and f(Q(t)) is the pdf of Q(t).

The pdf (13) for time-depth varying solute concentration generalizes to

$$\begin{aligned} f_c(c,z,t) = & \int_0^\infty f_c(c \mid \Phi \leq Q(t)) \cdot F_\Phi(Q(t))\ f(Q(t))\, dQ(t) \\ & + \int_0^\infty f_c(c \mid \Phi > Q(t)) \cdot [1 - F_\Phi(Q(t))] \cdot f(Q(t))dQ(t) \quad . \end{aligned} \tag{20}$$

Also, (14) generalizes to

$$f_c(c,z,t) = \int_0^\infty f_c(c,z,t \mid q_o)\, f(q_o)\, dq_o \tag{21}$$

where $f_c(c,z,t \mid q_o)$ is as defined in (14), and $f(q_o)$ is the pdf of random (constant in time) water application rate q_o. Expressions (15), (16) and (17) for various cases are also generalized similarly by unconditioning the conditional probability distributions by the pdf of Q(t).

The theoretical work, described above for the pdf of cumulative water content $\Phi(z,t)$ and for the pdf of solute concentration C(z,t) at field scale was tested by Monte Carlo simulations. For this purpose, the mean and covariance functions of the soil moisture content $\theta(z,t)$ which appear as the basic parameters in all probability distributions, were obtained from the field experiments, performed at U.C. Davis field site during this project. Using these data it was possible to show that for the drainage experiments, performed at U.C. Davis field site, the mathematical condition

(10a) for the complete validity of the approximate pdf (9) for $\Phi(z,t)$ always holds. Therefore, for the drainage experiments held at U.C. Davis field site, (9) is an exact solution for the pdf of $\Phi(z,t)$. Using the field experimental results for the mean and covariance functions of $\theta(z,t)$ and for the initial and boundary conditions for moisture flows, the pdf (9) which was theoretically derived from the stochastic vertical convective solute transport SPDE system (1), (2c), (2d), (3a) and (3b) was compared against corresponding Monte Carlo simulations of the same pdf as function of time and depth. The comparison results were very satisfactory. This comparison verifies the validity of the theoretical solutions to the pdf of time-depth nonstationary vertical convective solute transport in field soils.

III. PRINCIPAL FINDINGS AND SIGNIFICANCE

In this project first the implicit deterministic continuum solution of the vertical convective transport of a conservative solute in the vadose was obtained under both depth-dependent initial and time-dependent solute concentration conditions and general soil moisture initial and boundary conditions (equation (3)). Then an explicit deterministic continuum solution to this problem was obtained by keeping the solute concentration IC and UBC general but specializing the soil moisture IC and UBC to constants. This solution was then verified by numerical solutions of the same problem. If both the initial and boundary conditions for soil moisture flows and solute transport were deterministic and the soil profile was perfectly homogeneous at field scale, then the provided solution could be used to calculate the solute concentrations as function of time and soil depth under various initial soil contamination conditions, followed by various time-varying pollution loads on the soil surface.

However, at field-scale the soils are heterogeneous, thereby rendering the soil moisture flows a stochastic process. Furthermore, the water application rates at soil surface are in general uncertain, thus introducing a second source of stochasticity to soil moisture flows and solute transport. In this project an almost exact ensemble probability distribution function of solute travel time for time-depth nonstationary stochastic vertical convective solute transport within heterogeneous field-scale soils which also have statistically heterogeneous vertical soil profiles, unsteady, nonuniform moisture flows, and uncertain water application rates, was derived directly from the convective transport stochastic PDE under general depth-varying initial and time-varying boundary conditions (equations (19) and (11)). Validity of the approximation was verified by experimental results at U.C. Davis field site which showed that the approximate solution is exact for this field site. For the agricultural industry, irrigation specialists, and agencies (such as California WRCB) which are monitoring contaminant levels in field-scale soils, this probability distribution quantifies the risks of contaminant migration as function of soil depth and time, starting from an initial contaminant concentration profile in the soil and proceeding with known contaminant loads in time from the soil surface. Another useful tool which can also be utilized for such risk computations, is the ensemble pdf of solute concentration as function of soil depth and time for stochastic vertical convective solute transport within heterogeneous (stationary along the horizontal plane but nonstationary with respect to depth due to statistical heterogeneity of soil profile) field-scale soils under both deterministic (equation (14)) and uncertain (equation (21)) water application rates that was derived directly from the convective transport stochastic PDE under depth-varying initial and time-varying boundary concentration conditions. This derived pdf was verified by Monte Carlo simulation solutions of the convective transport stochastic PDE under parameters which were estimated from the experimental data at U.C. Davis field site. Various versions of the ensemble pdf of solute concentrations as function of time and depth for field-scale heterogeneous soils under various practical solute load scenarios and general IC and UBC soil moisture flows were also derived. Using these ensemble pdfs of solute concentrations as function of time and depth in field-scale heterogeneous soils it will be possible for California agricultural industry and state agencies to quantify the risks of contamination of the field-scale soils starting from an initial contaminant concentration profile with respect to soil depth and proceeding with known contaminant loads in time from the soil surface under certain or uncertain water application rates.

IV. PUBLICATIONS AND PRESENTATIONS

1. Kavvas, M.L., R.S. Govindaraju, D.E. Rolston, D. Or and J. Biggar, J. 1991. On the stochastic pollution transport equations. Invited paper. *Proceedings of Averaging methods: Genesis of Transport Equations in Porous Media, Effective Coefficients and Changes of Scale,* Special Session, held during the *International Seminar on Heat and Mass Transfer in Porous Media,* Dubrovnik, Yugoslavia, May 20-24.
2. Govindaraju, R.S., D.Or., M.L. Kavvas, D.E. Rolston, and J.W. Biggar. 1992. Applicability of simplified physical models for unsaturated water flow under large parameter uncertainty. *Water Resources Research.* In press.
3. Govindaraju, R.S., M.L. Kavvas, D.E. Rolson, D. Or and J. Biggar. 1991. Probabilistic solution of vertical unsaturated water flow under parameter uncertainty. In the workshop *Characterization of Transport in the Vadose Zone,* Tucson, AZ, April 2-5.
4. Kavvas, M.L., R.S. Govindaraju, D.E. Rolston, D. Or and J. Biggar. 1991. Ensemble average equation for time-space nonstationary stochastic pollution transport in soils. In the workshop *Characterization of Transport in the Vadose Zone,* Tucson, AZ, April 2-5.
5. Govindaraju R.S., D. Or, M.L. Kavvas, D.E. Rolston and J. Biggar. 1991. Use of simplified models under large variability in hydraulic properties. in *ASA-CSSA-SSSA annual Meeting,* Denver, CO, Oct. 27-Nov. 1.
6. Kavvas, M.L., R.S. Govindaraju, A. Karakas, D. Rolston, J. Biggar and D. Or. 1991. Probability distributions of nonstationary vertical convective transport in soils: I. Theory. *American Geophysical Union Fall Conference,* December, San Francisco.
7. Govindaraju, R.S., M.L. Kavvas, A. Karakas, D. Rolston, J. Biggar and D. Or. 1991. Probability distributions of nonstationary vertical convective transport in soils: II. Applications. *American Geophysical Union Fall Conference,* December, San Francisco.

V. REFERENCES

Biggar, J.W. and D.R. Nielsen, 1976. Spatial variability of the leaching characteristics of a field soil, W.R.R., 12(1), 78-84.

Bresler, E. and G. Dagan, 1979. Solute dispersion in unsaturated heterogeneous soil at field scale: II. Applications, Soil Sci. Soc. Am. J., 43, 467-472.

Bresler, E. and G. Dagan, 1981. Convective and pre scale dispersive transport in unsaturated heterogeneous fields, W.R.R., 17, 1683-1693.

Bresler, E. and G. Dagan, 1983. Unsaturated flow in spatially variable fields, 3. Solute transport models and their application to two fields, W.R.R., 19(2), 429-435.

Butters, G.L. and W.A. Jury, 1989. Field scale transport of bromide in an unsaturated soil, 2. Dispersion modeling, W.R.R., 25, 1583-1589.

Dagan, G. and E. Bresler, 1979. Solute dispersion in unsaturated heterogeneous soil at field scale: I. Theory, Soil Sci. Soc. Am. J., 43, 461-467.

Destouni, G., 1992. The effect of vertical soil heterogeneity on field scale solute flux, W.R.R., 28 (5), 1303-1309.

Jury, W.A., 1982. Simulation of solute transport using a transfer function model, W.R.R., 18(2), 363-368.

Jury, W.A., L.H. Stolzy, P. Shouse, 1982, A field test of the transfer function model for predicting solute transport, W.R.R., 18(2), 369-375.

Kavvas, M.L. and R.S. Govindaraju, 1991. Physics-based probability distributions of overland flows: 1. Theory, Stoch. Hydrol. Hydraul., 5, 89-104.

Nielsen, D.R., J. Biggar and K.T. Erh, 1972, Spatial variability of field-measured soil-water properties, Hilgardia, 42(7), 215-259.

Russo, D., 1991, Stochastic analysis of simulated vadose zone solute transport in a vertical cross section of heterogeneous soil during nonsteady water flow, W.R.R., 27(3), 267-283.

Russo, D., and G. Dagan, 1991, On solute transport in a heterogeneous porous formation under saturated and unsaturated water flows, W.R.R., 27(3), 285-292.

Simmons, C.S., 1982, A stochastic-convective transport representation of dispersion in one-dimensional porous media systems, W.R.R., 18(4), 1193-1214.

Sposito, G., W.A. Jury and V.K. Gupta, 1986, Fundamental problems in the stochastic convection-dispersion model of solute transport in aquifers and field soils, W.R.R., 22, 77-88.

TRAINING ACCOMPLISHMENTS

Name	Training Category	Training Level
R.S. Govindaraju	Civil Engineering	Post-Ph.D.
John Marion	Water Science	M.S.
Carl Klook	Ecology	M.S.
Tom Koos	Water Science	M.S.