

UNCERTAINTY IN LEACHING POTENTIAL OF NONPOINT SOURCE POLLUTANTS WITH APPLICATION TO A GIS

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ABSTRACT

This paper presents a stochastic framework for the assessment of groundwater pollution potential of nonpoint source pesticides. A conceptual relationship is presented that relates seasonally averaged groundwater recharge to soil properties and depths to the water table. The analytical relationship shows a linear association with the soil saturated hydraulic conductivity, and predicts less recharge for shallower water tables. A modified index model for pesticides mass emissions in the soil is developed, which accounts explicitly for biochemical degradation in the mobile and immobile soil-water zones and losses by volatilization and crop uptake. The index model shows that the effect of nonequilibrium transport on the residual mass emissions is dependent on ratio of the mass transfer coefficient and the first-order degradation rate in the immobile phase. The stochastic framework utilizes first-order approximations of the mean and variance of each of the recharge and the residual mass emissions in the soil. Soil and chemical properties and related environmental factors, which affect the fate and transport of pesticides, and the depth to the water table are modeled as random variables. The environmental-fate models are integrated with a GIS, and the stochastic framework is applied to assess potential nonpoint-source vulnerability of shallow groundwater to the pesticide dicamba in Mid-Atlantic coastal plain agricultural watersheds. It is shown that recharge estimates on the basis of the SCS abstraction method resulted in lower expected dicamba concentrations in groundwater, than when leaching is based on the conceptual model. This may be attributed to the fact that in the former leaching is averaged over the soil hydrologic groups, whereas in the latter leaching reflects the spatial variability of the soil types and environmental factors, including the depth to the water table. In the analysis, biochemical degradation of dicamba is ignored below the root zone and the vulnerability results were based on a single application of 2.5lb/acre. The first-order estimates of the variance of dicamba mass emissions and estimated groundwater concentrations, were of order of magnitude of their respective means and greater. While some of the mean groundwater concentrations showed significant residual levels of dicamba, these values however should be viewed as subject to high uncertainty. Given the expected uncertainties in the input data and model errors, regulatory decisions and environmental land-use planning should take into account estimates of the uncertainties (e.g., variances) associated with predictions of groundwater vulnerabilities.

INTRODUCTION

Pesticides are sited among the most common nonpoint source pollutants (NPS) pollutants, which threaten sustainable agriculture and constitute a great threat to surface and subsurface drinking water resources (*Loague, et al.*, 1998). There is a heightened concern among the public and policy makers that soil and groundwater resources are continuously threatened and degraded by improper use and mismanagement of agrichemicals. Proper land-use

planning can circumvent potential harmful environmental impacts, such as groundwater contamination. Conceptual environmental-fate models offer a promising avenue for the management of agrochemicals by forecasting the movement of NPS pollutants and identifying potential loss pathways in soil, with the objective of preventing pollution potential beforehand.

Modeling NPS pollutants, however, is a complex and a demanding task. The volume of information required for temporal and spatial characterization of the parameters and variables needed, in even the simplest conceptual models of solute transport in the vadose zone, is tremendous (*Crowin et al.* 1997). A Geographic Information System (GIS) can be used as an effective tool for the management of volumes of data of spatial and temporal nature, and when linked with environmental-fate models would make spatial data available for environmental analysis (*Hoogeweg and Hornsby*, 1995). It is a tool designed to acquire, store, analyze, and display spatial information. The display of spatially related information by a GIS can be very useful, especially in identifying spatial patterns of significant values to regulatory agencies and policy makers for planning purposes. *Khan and Liang* (1989) were among the first who applied GIS to create groundwater contamination likelihood maps for Oahu, Hawaii. They used the attenuation factor AF of *Rao et al.* (1985) and *Mahmood and Sims* (1986) to assess the relative likelihood of groundwater contamination. Rather than using complex mathematical models that describe the transport of pesticides in subsurface systems (e.g., *Wagenet and Huston*, 1986; and *Carsel et al.*, 1984), the simpler AF models (commonly referred to as indices) are more favorable due to lack of independent measurements for parameters required in the complex models. *Kleveno et al.* (1992) evaluated the attenuation factor (AF) by comparing it with the more rigorous and conceptual pesticide root zone model PRZM (*Carsel et al.*, 1984). They indicated that AF compared well to PRZM in ranking the relative mobility of a selection of pesticides, in heterogeneous soil and under conditions of variable recharge. *Hoogeweg and Hornsby*, (1995) created a graphical user interface for an integrated GIS/environmental-fate models to facilitate access to multiple fate and transport models and the evaluation of pesticide effects on groundwater quality. *Loague et al.* (1995) suggested the use of mobility indices as physical factors in a regional integrated assessment approach (RIA) using GIS.

This paper emphasizes four particular aspects of groundwater vulnerability assessment including application to a case study using a GIS. First, since recharge is the only mechanism responsible for the transport of pollutants from the source to the receptor, its importance is recognized and a new conceptual relationship is presented for the estimation of local temporally averaged (quasi-steady) groundwater recharge. The relationship is based on soil-water retention model of *Campbell* (1974) and requires the knowledge of depth to the water table. Secondly, mass fraction emission models are presented, which describe fate and transport of pesticides in soil, including the effect of nonequilibrium transport due to mobile-immobile solute exchange by diffusion. It is worth noting that the utility of existing indices (e.g., *Rao et al.*, 1985; and *Mahmood and Sims*, 1986) is based on field based pesticides half-life values, and their use under different field and climatic conditions may therefore be subject to uncertainty. Since organic compounds, such as pesticides, differ in their characteristics and their behavior in the environment, then the ability to quantify the relationship between their half-lives and the different loss pathways may reduce uncertainties and improve model predictions. The relationship between effective (field scale) half-life and biochemical degradation, volatilization, crop uptake, and losses in immobile water regions will be addressed. Thirdly, a stochastic framework, using first-order analysis, will be developed for the estimation of means and variances of the recharge and mass fraction emissions below the root zone, in terms of uncertainties in model input parameters. Assessment models, such as the AF, are based upon soil, chemical, hydrologic, and environmental data that are usually sparse and highly uncertain. Therefore, the impact of uncertainty of data, including errors in the conceptual model, should be quantified as a measure of the reliability of predicted assessment maps that are based on fixed input parameters (e.g., *Loague et al.*, 1995). The methodology will be applied to assess shallow groundwater vulnerability to the pesticide dicamba in paired agricultural watersheds in the Mid-Atlantic coastal plain. The objective of the stochastic framework is to establish the extent to which the mean dicamba mass emissions are reliable predictions of actual assessment maps of groundwater vulnerability. GIS displays of an environmental-fate model outputs should be viewed with uncertainty and therefore has no real utility without a corresponding map of associated uncertainties (*Loague et al.*, 1998).

DETERMINISTIC ANALYSIS

Conceptual Model For Quasi-Steady Recharge

In this section we develop an equation, which describes quasi-steady percolation below the root zone, as a function of average depth to the water table and uniform (depth-averaged) soil properties. The Buckingham-Darcy flux law can describe the flow in the unsaturated zone (Bear, 1972):

$$q(z, t) = K(\psi) \frac{\partial \psi}{\partial z} + K(\psi) \quad (1)$$

in which, $q(z, t)$ is the flux per unit area [m/d]; $K(\psi)$ is unsaturated hydraulic conductivity [m/d]; ψ is the suction head (negative of matric potential)[m]; z is the depth below the surface [m](Fig. 1); and t denotes time [d]. Note that in (1) q follows the sign convention of assuming a positive value when it is defined downward.

We first define the time-average operator $\langle \rangle$ as

$$\langle f(t) \rangle = \frac{1}{T} \int_0^T f(\tau) d\tau \quad (2)$$

in which $f(t)$ is some function of time, and T is a time interval over which (1) will be averaged and quasi-steady q is defined. If we fix t at an arbitrary value $t = \tau$, $0 \leq \tau \leq T$, and replace the partial derivative in (1) with a total derivative (i.e., denoting derivative only with respect to z at fixed t), then Eq. (1) can be written as

$$\frac{dz}{d\psi_\tau} = \frac{1}{q_\tau / K(\psi_\tau) - 1} \quad (3)$$

in which $\psi_\tau = \psi(z; t=\tau)$ and $q_\tau = q(z; t=\tau)$ are functions of z for a fixed t .

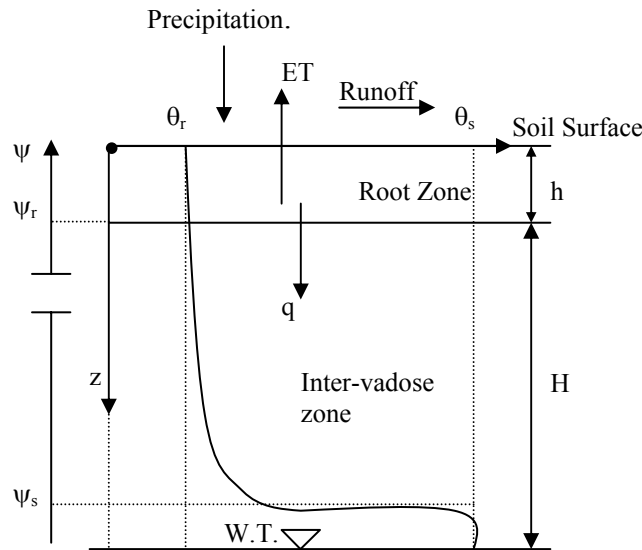


Fig. 1 Illustration of water balance in unsaturated zone.

Because abstractions due to roots uptake and evaporation are assumed to occur only in the root zone, q can be assumed to be independent of z . The integration of Eq. (3) from the soil surface to the water table, $z = h$ to $z = H(\tau)$, yields

$$\int_h^{h+H(\tau)} dz = \int_{\psi_r(\tau)}^0 \frac{d\psi_\tau}{q_\tau / K(\psi_\tau) - 1} \quad (4)$$

where H is the depth to the water table below the root zone at $t = \tau$ [m], and ψ_r is the suction head at the interface between the root zone and the intermediate vadose zone at $t = \tau$ [m].

The relationship between the hydraulic conductivity and suction head for different soils may be describe by the following equation (*Campbell, 1974*)

$$K(\psi) = K_s \left(\frac{\psi}{\psi_s} \right)^{-a}, \quad a = \frac{b}{2b + 3} \quad (5)$$

where K_s is the saturated-soil hydraulic conductivity [cm/day]; ψ_s = saturation suction [cm]; and b is an empirical parameter. Equation (5) is based on the following moisture characteristic

$$\psi = \psi_s \left(\frac{\theta}{\theta_s} \right)^{-b} \quad (6)$$

in which θ is the soil volumetric water content and θ_s is the saturated water content. A data set for the parameters K_s , θ_s , and b for different soils can be obtained from *Clapp and Hornberger (1978)*. It should be noted that Eq. (6) is not accurate near saturation (*Campbell, 1974*). The latter authors proposed a short parabolic section near saturation to represent gradual air entry. The substitution of right-hand side of (5) for K in (4) and the application of the time-average operator $\langle \rangle$ to the resulting integral equation yields

$$\langle H(\tau) \rangle = \left\langle \int_0^{\psi_r(\tau)} \frac{d\psi}{1 - (q(\tau) / K_s)(\psi / \psi_s)^a} \right\rangle \quad (7)$$

Where we have dropped the subscript τ notation from ψ in the integrand because ψ is a dummy variable, and replaced q_τ with $q(\tau)$ to denote a functional relationship with respect to τ . To the first order, the approximate integral equation which governs quasi-steady recharge to the water table is given by:

$$H = \int_0^{\psi_r} \frac{d\psi}{1 - (q / K_s)(\psi / \psi_s)^a} \quad (8)$$

in which $H = \langle H(\tau) \rangle$, $\psi_r = \langle \psi_r(\tau) \rangle$, and $q = \langle q(\tau) \rangle$. Equation (8) is a first-order approximation to (7), since the left-hand side of the latter is expressed in terms of time-averaged variables. The truncated higher order terms are expected to be significant for large temporal variations in $H(\tau)$, $\psi(\tau)$, and $q(\tau)$, and can be quantified using second-order analysis in terms of the variances of fluctuations of these variables (second moments). However, this is beyond the scope of this paper. Thus, Eq. (8) will be used to develop an approximate closed-form solution for quasi-steady q in a uniform soil profile. After a simple transformation and expanding the integrand in (8) using Taylor series, it can be shown that

$$q = \frac{2a+1}{2a+2} \left(\frac{\psi_s}{\psi_r} \right)^a K_s \left(\sqrt{1 + 4 \frac{(a+1)^2}{2a+1} \left(\frac{H}{\psi_r} - 1 \right)} - 1 \right) \quad (9a)$$

If the following conditions are satisfied

$$\frac{q}{K_s} \left(\frac{\psi_r}{\psi_s} \right)^a < 1, \quad \text{and} \quad H \geq \psi_r \geq \psi_s \quad (9b)$$

It's worth noting that this equation is consistent with the solution of the Buckingham-Darcy equation at equilibrium conditions, since both predict that $\psi(0) = \psi_r = H$ when $q=0$. The condition $\psi_s \leq \psi_r$ is necessary because Eq. (5) requires that $\psi_s \leq \psi$ for $K(\psi) \leq K_s$ to be a valid definition of unsaturated conductivity. Equation (9) is valid when the water table has risen in response to a recharge process; therefore, it's not valid for the specific case where a decreasing recharge rate causes a declining water table. This equation predicts a linear association with the saturated hydraulic conductivity and greater recharge for deeper water table, because greater recharge is required to elevate deeper water tables. An interesting point may be that (9) provides an indirect mean for the estimation of percolation below the root zone. That is, it rests upon the response of the water table to a net recharge process rather than flow balance at the soil surface and the root zone. Thus, it may be used in case of uncertainty in irrigation practices and actual evapotranspirative losses.

Leaching of Pesticides in the Soil

In this section we present a physically based relationship for leached mass fractions below the root zone and residual emissions to the water table. The relationship considers the effects of biochemical degradation, dispersion, and mobile-immobile nonequilibrium solute transport exclusively. Figure 2 illustrates the system under consideration.

Leached mass fraction of a pesticide mass M_0 incorporated in a thin surficial soil layer may be described by the following equation (Hantush *et al.*, 1998)

$$M_r(z) = M_0 e^{-\frac{P_r}{2} \left\{ \sqrt{1 + 4 \frac{T_r}{P_r} \frac{\ln(2)}{\lambda_r^m} (1 + \mu + \phi_r)} - 1 \right\} \frac{z}{h}} \quad (10)$$

where

$$\phi_r = \frac{\beta(\alpha / k_r^{im}) \lambda_r^m}{(\alpha / k_r^{im}) + \beta \lambda_r^{im}} \quad (11)$$

$$\mu = \frac{(FS + \sigma / h) \lambda_r^m}{\ln(2) R_r^m \theta_r^m} \quad (12)$$

where $\sigma = \kappa_r^m K_H D_g / d$ is the volatilization rate coefficient [m/d]; κ_r^m = volumetric air content in the mobile phase; K_H = dimensionless Henry constant; S = transpiration rate [day^{-1}]; F = transpiration-stream concentration factor; D_g = gaseous diffusion coefficient [m^2/d]; h is average depth of the root zone [m]; d = thickness of air boundary layer on soil surface [m]; $\beta = \theta_r^{im} R_r^{im} / \theta_r^m R_r^m$ may be referred to as the capacity ratio; $k_r^m = \ln(2) / \lambda_r^m$ and $k_r^{im} = \ln(2) / \lambda_r^{im}$ are the degradation rates in the mobile and immobile phases, respectively [day^{-1}]; θ_r^{im} is the volumetric immobile water content; θ_r^m is the volumetric mobile water content; α is a mass transfer coefficient [d^{-1}]; R_r^m and R_r^{im} are the retardation factors in the mobile and immobile water regions, respectively; $D_r^m = (\kappa_r^m / \theta_r^m) K_H D_g + D_z$ is the effective (multiphase) dispersion coefficient in the mobile region [m^2/d]; $P_r = h(\bar{v} / \theta_r^m) / D_r^m$ is the soil root-zone Peclet number; $T_r = h R_r^m / (\bar{v} / \theta_r^m)$ is the apparent residence time in the root zone [day]; $\bar{v} = q + (ET / 2)$ is the average flux in the root zone [m/d]; and ET is evapotranspiration rate per unit area [m/d]. Equations (10-12) describe the relationship between the leached mass emissions of organic compounds below the root zone and losses due to biochemical degradation in the mobile and immobile phases, volatilization, and crop uptake, and the relationship with soil and chemical properties, and related environmental factors. It extends the leached-fraction expression of Van der Zee and Boesten (1991) to account for the effect of crop uptake, volatilization, and in particular, nonequilibrium solute transport. Diffusive vapor losses from the immobile zone are ignored in (10).

Partitioning into the vapor phase in the immobile zone, however, is allowed and can be accounted for in the immobile-phase retardation factor $R_r^{im} = 1 + (f_{im} \rho_b K_d + \kappa_u^{im} K_H) / \theta_r^{im}$, in which f_{im} and κ_u^{im} are the fraction of soil bulk density and volumetric air contents in immobile water regions, respectively. And $R_r^m = 1 + (f_m \rho_b K_d + \kappa_u^m K_H) / \theta_r^m$, in which f_m and κ_u^m are the fraction of soil bulk density and volumetric air content in conductive pore regions (mobile phase), respectively.

Note that that nonequilibrium transport due to diffusion into immobile-water regions has impact on the integrated solute flux, $M_r(z)$, only when environmental conditions are conducive for biodegradation in the immobile phase: $\phi_r \rightarrow 0$ as $\lambda_r^{im} \rightarrow \infty$ ($k_r^{im} \rightarrow 0$). In the absence of degradation in regions of stagnant water, such as intra-aggregate pores in aggregated soils, the fraction of the solute in the immobile phase would ultimately diffuse back into the mobile phase and leaves the root zone. The extent to which nonequilibrium transport affects the total mass available for leaching is related to the ratio of the mass transfer rate coefficient α to the decay rate constant in the immobile zone k_r^{im} , as (11) indicates.

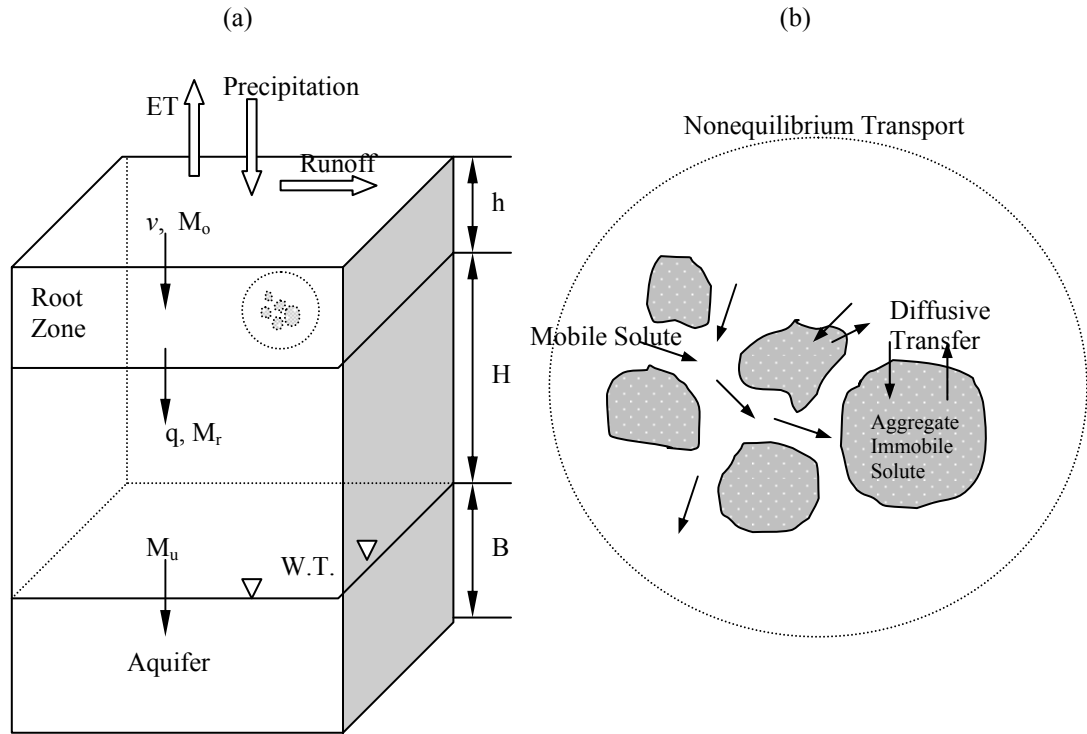


Fig. 2 (a) Illustration of a soil-aquifer system; and (b) fate and transport in mobile-immobile phase.

Eq. (10) can also be used to describe leaching and transformation in the intermediate vadose zone, assuming negligible diffusive vapor transport and that losses are limited to biochemical degradation:

$$M_u(z) = M_r(h) e^{-\frac{P_u}{2} \left[\sqrt{1 + 4 \frac{T_u}{P_u} \frac{\ln(2)}{\lambda_u^m} (1 + \phi_u)} - 1 \right] \frac{z-h}{H}} \quad (13)$$

in which ϕ_u is given by (11) with the associated parameters defined in the intermediate vadose zone; $P_u = H(q/\theta_u^m)/D_u^m$ is the intermediate vadose soil Peclet number; and $D_u^m = (\kappa_u^m/\theta_u^m)K_H D_g + D_z$, the effective liquid-phase diffusion coefficients in the intermediate vadose zone [m^2/d].

The half-life parameters λ_r^m and λ_u^m in (10) and (13) are understood to account for biochemical degradation. Half-life values estimated in the field may integrate all possible loss pathways. Thus, their use in (10) and (13) may seriously overestimate actual losses in the field. It is difficult to verify whether the values that are reported in the literature are estimated under laboratory or field conditions. Since values for pesticides degradation half-life in subsoils and ground water are scarce (Rao and Hornsby, 1989) and subject to uncertainty, the rational approach is to consider $\lambda_{eff} = \lambda_r^m / [1 + \mu + \phi_r]$ a random variable. In reality estimates of recharge, soil parameters, and other environmental factors are subject to uncertainty and they display complex spatial and/or temporal variability. And a stochastic framework, in this case, is necessary for a meaningful vulnerability assessment scheme.

UNCERTAINTY ANALYSIS

First-Order and Second-Order Analysis

Let $f(\mathbf{X})$ be a continuous and differentiable function of a set of N random variables $\mathbf{X} = (x_1, x_2, x_3, \dots, x_N)$, then it can be shown by expanding $f(\mathbf{X})$ in a Taylor series about the mean values $E(x_1) = \bar{x}_1$, $E(x_2) = \bar{x}_2$, ..., $E(x_N) = \bar{x}_N$, where $E(*)$ denotes the expectation operator, that the second-order approximation of the mean of $f(\mathbf{X})$ is given by (Ang and Tang, 1975)

$$\overline{f(X)} = E[f(X)] = f(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N Cov(x_i, x_j) \frac{\partial^2 f(\bar{X})}{\partial x_i \partial x_j} \quad (14)$$

and the variance to the first-order is given by

$$Var[f(X)] = E[f(X) - \overline{f(X)}]^2 = \sum_{i=1}^N \sum_{j=1}^N \frac{\partial f(\bar{X})}{\partial x_i} \frac{\partial f(\bar{X})}{\partial x_j} Cov(x_i, x_j) \quad (15)$$

In which the partial and mixed-partial derivatives are evaluated at the mean vector $\bar{X}$. In the analysis below we will consider the following random vector $\mathbf{X} = (f_{oc}, K_{oc}, H, \lambda, b, \theta_s, \psi_s, K_s)$. Cross correlation among these parameters is ignored due to lack of data that support otherwise.

Uncertainty Analysis of Recharge

The mean recharge $\bar{q}$ can be approximated to the first-order by applying Eq. 14 to Eq. 9,

$$\bar{q} = \frac{2\bar{a}+1}{2\bar{a}+2} \left(\frac{\bar{\psi}_s}{\bar{\psi}_r} \right)^{\bar{a}} \bar{K}_s \left(\sqrt{1 + 4 \frac{(\bar{a}+1)^2}{2\bar{a}+1} \left(\frac{\bar{H}}{\bar{\psi}_r} - 1 \right)} - 1 \right), \quad \bar{a} = \frac{\bar{b}}{2\bar{b}+3} \quad (16)$$

which is (9) evaluated at the means of all random parameters. In equation (6), we have assumed ψ_r to be deterministic and at or greater than field capacity ($-1/3$ bar = 340 cm).

The first-order approximation to the variance of q is given by

$$Var(q) = \left(\frac{\partial q}{\partial K_s} \right)^2 Var(K_s) + \left(\frac{\partial q}{\partial \psi_s} \right)^2 Var(\psi_s) + \left(\frac{\partial q}{\partial a} \frac{da}{db} \right)^2 Var(b) + \left(\frac{\partial q}{\partial H} \right)^2 Var(H) \quad (17)$$

in which partial derivatives are evaluated at $\bar{X} = (\bar{f}_{oc}, \bar{H}, \bar{\lambda}, \bar{b}, \bar{\theta}_s, \bar{\psi}_s, \bar{K}_s)$.

$\text{Var}(\psi_s)$ and $\text{Var}(b)$ can be obtained from the literature (*Clapp and Hornberger, 1978*). $\text{Var}(H)$ is inferred from random variations of H in time at each observation well, and an average variance is considered for each soil hydrologic group (A,B,C,D), by averaging the variance of the wells located in each hydrologic group. The variance of K_s however is not accounted for in this study. It should be emphasized that $\text{Var}(H)$ is expected to vary in space due to recharge and other effects such as boundary conditions, and that the influence of unknown pumping activities and unknown intensive irrigation activities may result in biased estimates for $\text{Var}(H)$.

We will compare in the application section recharge estimates based on the local equation (16) and estimates of recharge using the SCS method (*Chow et al., 1988*). The latter method relies on the Hydrological groups of the soil map, whereas the former requires the knowledge of local soil type and related properties. It is important to note that recharge analysis on the basis of Eq. (9) does not require direct estimates of precipitation, abstractions, irrigation, and evapotranspiration (ET). Instead, it relies on the response of the water table to the net balance in the form of deep percolation. Its applicability therefore depends on the availability of measurements of H , where the water table fluctuates only in response to the recharge process (i.e. precipitation and irrigation). Note that Eq. (17) relates the variance of net recharge q directly to the temporal variability of the water table fluctuations, and not to the variability of climatic factors, including ET. Estimation of recharge variance using the direct method would have been difficult due to uncertainty in irrigation rates and events, and difficulties in the estimation of the variance of evapotranspiration, due to lack of real-time measurements. Evapotranspiration (ET) is usually estimated using quasi-empirical methods, which rely on energy balance and heat transfer concepts, and empirical crop factors. Thus, estimation of the variance of ET requires continuous measurements in time. A modification of (9) is required for the case of a stratified soils below the root zone and be achieved using effective soil parameters (e.g., *Gelhar, 1993*).

Stochastic Analysis of Pesticides Leaching

As mentioned earlier, we consider a random half-life parameter λ rather than $\lambda_{eff} = \lambda_r^m / [1 + \mu + \phi_r]$, which accounts for the individual effects of all possible loss-pathway, including the parameters μ and ϕ_r . This is mainly for two reasons. First, the uncertainty in reported half-life values in the literature. And secondly, while the impact of diffusive transfer into immobile zones can be significant, the lack of information regarding the environmental factors and geometric properties, which are associated with or necessary for characterizing the soil mobile immobile zones, makes it difficult to obtain meaningful estimates for the parameter ϕ_r . While the treatment of nonequilibrium transport of pesticides in the soil is important, especially in aggregated soils (e.g., *van Genuchten and Wierenga, 1976*), it is, however, beyond the scope of this paper. We will ignore biodegradation in the intermediate-vadose soil and limit our analysis to leaching below the biologically active root zone, at $z = h$. Biodegradation is likely to be much less significant in the root zone where the likelihood of having a biotic degradation is small (*Rao and Hornsby, 1989*).

Again, we make use of (14) to obtain second-order approximation of the leached mass fraction in (10):

$$\overline{M_r} = M_o e^{-\frac{P_r}{2} \left\{ \sqrt{1 + 4 \frac{\overline{T_r}}{P_r} \frac{\ln(2)}{\overline{\lambda}}} - 1 \right\}} + \frac{1}{2} \frac{\partial^2 M_r}{\partial \lambda^2} \text{Var}(\lambda) + \frac{1}{2} \frac{\partial^2 M_r}{\partial T_r} \text{Var}(T_r) \quad (18)$$

in which the over-bar notation implies the ensemble mean and the partial derivatives are evaluated at the mean parameters $(\overline{\lambda}, \overline{T_r})$. The variance can be obtained by applying (15) to (10) evaluated at $z = h$,

$$\text{Var}(M_r) = \frac{\ln^2(2) \overline{M_r}^2}{\overline{\lambda}^2 \left(1 + 4 \ln(2) \frac{\overline{T_r}}{P_r \overline{\lambda}} \right)} \left(\text{Var}(T_r) + \left(\frac{\overline{T_r}}{\overline{\lambda}} \right)^2 \text{Var}(\lambda) \right) \quad (19)$$

where

$$Var(T_r) = \left(\frac{\overline{T_r}}{\bar{v}} \right)^2 Var(q) + \left(\frac{h}{\bar{v}} \rho_b^2 \overline{f_{oc}} \right)^2 Var(K_{oc}) + \left(\frac{h}{\bar{v}} \rho_b^2 \overline{K_{oc}} \right)^2 Var(f_{oc}) \quad (20)$$

In Eqs. (18)-(20), we assumed that dispersion is predominantly mechanical mixing; i.e., $P_r = h/\alpha_L$, where α_L is the longitudinal dispersivity [m]. Thus, P_r is considered deterministic for a fixed h . Also, because the variance of ET cannot be estimated directly for the reasons explained above, it is assumed deterministic and, thus, $Var(\bar{v}) = Var(q)$ follows directly from $\bar{v} = q + (ET/2)$.

In the above analysis we adopt the definition of the contamination potential of a pesticide as “the likelihood of a chemical to pass through the biologically active surface soil horizons (usually top 1 m),” (*Khan and Liang, 1989*). We therefore focused our analysis above on leaching below the root zone and assumed that $M_u = M_r$, on the basis that biological activity seldom extends below this zone (*Hillel, 1982*; and *Rao and Hornsby, 1991*). However, chemical reactions will further degrade some pesticides after leaching below the root zone (*Rao and Hornsby, 1991*), and further analysis of (13) in the intermediate vadose soil will be required..

Pesticides concentrations in ground water are estimated using the relationship

$$\overline{C_g} = \frac{\overline{M_u}}{n B} \quad (21)$$

in which $\overline{C_g}$ is the mean solute concentration in ground water [Kg/m^3]; n is the aquifer porosity, and B the thickness of contaminant plume [m]. The variance of C_g , thus, is given by

$$Var(C_g) = \frac{Var(M_u)}{n^2 B^2} \quad (22)$$

in which n and B are assumed to be constant.

APPLICATION WITH ARCVIEW GIS

Case Study: Mid-Atlantic Coastal Plain Agricultural Watershed

The study site (Locust Grove) is located in Kent County, Maryland, and covers approximately an area of 120 km^2 (Fig. 3). The site is composed of two agricultural watersheds that are drained by the Morgan Creek and the Chesterville Branch (Fig. 3). Both streams drain in to the Chester River, which lies along the southern boundary of Kent County, Maryland, and along the northeastern shore of the Chesapeake Bay. Agriculture dominates the landscape in the study area and most of the land there is used to grow corn and soybeans in an annual rotation with winter wheat. Riparian forested areas are marginal and restricted to strips along the two creeks and some of the land is used to grow ornamental trees. The soil in the study area is predominantly silt loam and to a lesser extent ranged from loam to sandy and gravelly loams. The area is underlain by the surficial (Columbia) aquifer, which consists of sand and gravel of fluvial origin.

ArcView GIS database is developed for the soil and land use properties using the soil survey of Kent County, Maryland (United States Department of Agriculture, Soil Conservation Service in cooperation with the Maryland Agricultural Experiment Station and the Kent Soil Conservation District, Issued January 1982). The database is complemented by soil hydraulic properties, including organic carbon fractions from available literature (*Ravi and Johnson, 1991*, and *Carsel et al., 1988*).

The pesticide chosen in this study is dicamba, which is among the most detected residues in the Delmarva Peninsula,

and commonly used for Wheat-barley-alfalfa and Soybeans (Koterba *et al.*, 1993). The results presented below (GIS maps) are not based on actual agricultural land use, rather, they represent the vulnerability of ground water to dicamba applied to soils that are suitable for growing winter wheat and small grains. A single application of 2.5 lb/acre is assumed in the simulated vulnerability maps. An average half-life value of 16 days and a standard deviation of 7 days are assumed for the short-lived dicamba (an Internet source provided by the ARS and the Natural Resources Conservation Service, currently available at the following web site address: <http://www.arsusda.gov/rsml/ppdb2.html>). The mean and variance of the organic carbon partition coefficient K_{oc} were estimated from dicamba database, using the same source: $\overline{K_{oc}} = 7.6 \text{ l/Kg}$ and $\sqrt{Var(K_{oc})} = 7.27 \text{ l/Kg}$. The plume thickness B in ground water is assumed to be 5 m and the porosity of surficial Columbia aquifer porosity n in the study site is considered to be 0.3 (Reilly *et al.*, 1994).

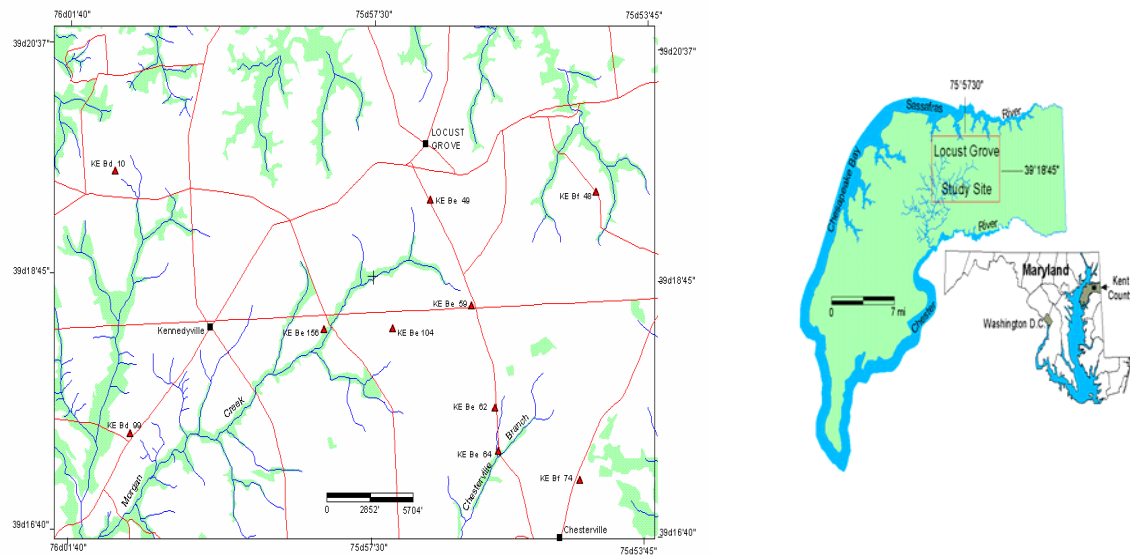


Fig.3 Geographical Location and detailed map of Locust Grove Study Site

Discussion of Results

Data for depths to water table are based on water levels in wells recorded in 1991, 1992 (source: Maryland Geological Survey), 1997, and 1998 (source: US Geological Survey, Maryland). Recorded water levels in Wells KE Be 49 and KE Be 62 (Fig. 3) from October 97 to June 98 are shown in Figs 4(a) and 4(b). In general, observed water table levels indicated an increasing trend toward a steady level, from the month of October to the month of June, which indicates a recharge activity. Figure 5(a) compares the theoretical recharge (Eq. 9, assuming ψ_s within standard deviations reported by Clapp and Hornberger (1978)) and estimates based on soil Hydrologic Classes using the SCS abstraction method and the method of Thornthwaite and Mather (1957). The SCS estimates are based on monthly record of precipitation obtained from Chestertown weather station. The estimates of q using Eq. (9) were made at several observation wells, some of which are shown on Fig. 3, based on depths to water table averaged over the same period of November to April, from 1991, 1992, and 1998 water table records. Those values of q in observation wells that are located in a given soil Hydrologic Class (A, B, C, and D) were averaged and compared in Fig. 5(a) to the value estimated for the same soil Class using the SCS abstraction and Thornthwaite and Mather

(1957) method (will be referred to as SCS hereafter). The apparent correspondence between the empirical and theoretical $\bar{q}$ in Fig. 5(a) indicates that local recharge estimated by (9) averaged over soil Hydrologic Classes may be consistent with the SCS recharge estimates. Thus, Eq. 9 may be used to estimate recharge at the local scale and as a function of local soil hydraulic properties and depth to the water table. And this may hold for relatively shallow water table in order to allow for meaningful time averages on which (9) is based.

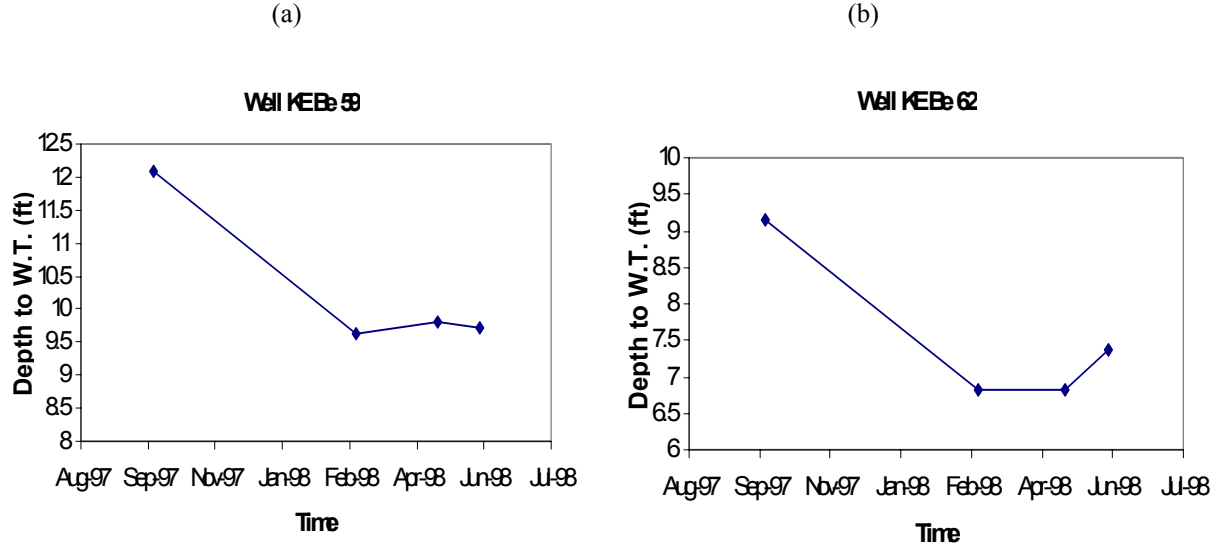


Fig.4 Records of Depth to water table in: (a) Well # KEB59; and (b) Well #KEB62

Figure 5(b) shows that soils in Chesterville Branch appear to be primarily class B, whereas they are primarily class C in Morgan Creek. Thus, cumulative infiltration based on the SCS method is expected to be less in the latter due to greater potential for surface runoff, i.e., more poorly drained. Low drainage capacity is attributed to a combination of shallow depth to the water table and lower infiltration capacity (*Philips and Bachman, 1996*). This is consistent with (9), which indicates smaller recharge, thereby greater potential for surface runoff for shallow depths to water table, H . It also predicts less q , thus, greater surface runoff for increasingly finer soils due to smaller saturated hydraulic conductivity K_s and lower infiltration capacity. As expected, Fig. 6(a) shows that recharge estimates using the SCS abstractions method corresponds with the soil pattern according to the Hydrological Classification in Fig. 5(b). The estimates of mean and variance of recharge ($\bar{q}$ and $\text{Var}(q)$) using Eqs. (16) and (17) are shown in Figs 7(a) and 7(b). Comparison with Fig. 6(a) shows that the SCS recharge estimates are over estimated by $\bar{q}$ (Eq. 16), however, both predicted a general pattern of relatively greater recharge on the east side and north of the Chesterville Branch and around the north (headwaters) of the western branch of Morgan Creek. Also, both predicted greater values around the north (headwaters) of the eastern branch of Morgan Creek. It is not clear if uncertainty in the kriged estimates of depths to the water table were responsible for the relatively lower estimate of $\bar{q}$ in an area of Class A (well drained) soil, which is located downstream in the western branch of Morgan Creek. Compare south-eastern corners of Figs 6(a) and 7(a)).

Given the relatively large values of $\text{Var}(q)$ in Fig. 7(b), the estimated mean recharge values in Fig. 7(a) are subject to great uncertainty. It is worth noting that depths to the water were based on highly variable digital elevation map and preliminary kriged estimates of H conditioned on the observed values. The standard deviations based on the first-order approximation in (17) are of the same order of magnitude of the estimated mean values, as Fig. 7(b) shows. This may be partially attributed to inaccurate kriged values of H and lack of sufficient temporal measurements of water levels needed to filter out deterministic trends, which resulted in significant values for $\text{Var}(H(t))$ as large as 10 m^2 . This underscores the need for more measurements of depths to the water table, especially in time, and a more

reliable strategy for the estimation of H , which is currently under investigation. In light of uncertainty in the vertical soil variability and lack of sufficient temporal records of water table fluctuations, further assessment and evaluation of the recharge relationship (9) is needed.

Figures 7(c-f) show first-order approximations to the mean and variance of each of dicamba mass emission to the water table, M_u , and the resulting concentration in ground water, C_g . Biochemical degradation is ignored in the intermediate vadose zone, and therefore $M_u = M_r$. This may be considered a worst case scenario, although it is based on a single application of dicamba of 2.5 lb/acre, and multiple applications are not uncommon. Figure 7(e) shows that significant portions of the study area, on the east and around Morgan Creek, displayed mean groundwater concentrations between 120 ppb and 144 ppb. These values are close to the Lifetime Health Advisory Level (HAL) of 200 ppb ($\mu\text{g/L}$ or 10^{-6} Kg/m^3) set for dicamba. We emphasize that the relatively greater variances in Figs. 7(d) and 7(f) are attributed to the large variances of the residence time in the root zone, $\text{Var}(T_r)$ (some values where of two orders of magnitude greater than the mean), Which are the result of relatively large variances of H and K_{oc} parameter. This is in spite of ignoring decay losses in the intermediate vadose zone. The coefficient of variation ($CV = \text{standard deviation} / \text{mean}$) for predicted dicamba concentration in ground water, $CV(C_g) = \sqrt{\text{Var}(C_g)} / \overline{C_g} = (.0783)^{1/2} / (0.000144) = 1887$ (see, Figs. 7(e) and 7(f)). This implies that, although few, the estimated mean dicamba concentrations may be subject to very high uncertainty. It is possible that first-order approximation of the variance highly overestimated the variance. It is also likely that uncertainty in depths to the water table and uncertainty in the above mentioned environmental factors were a contributing factor.

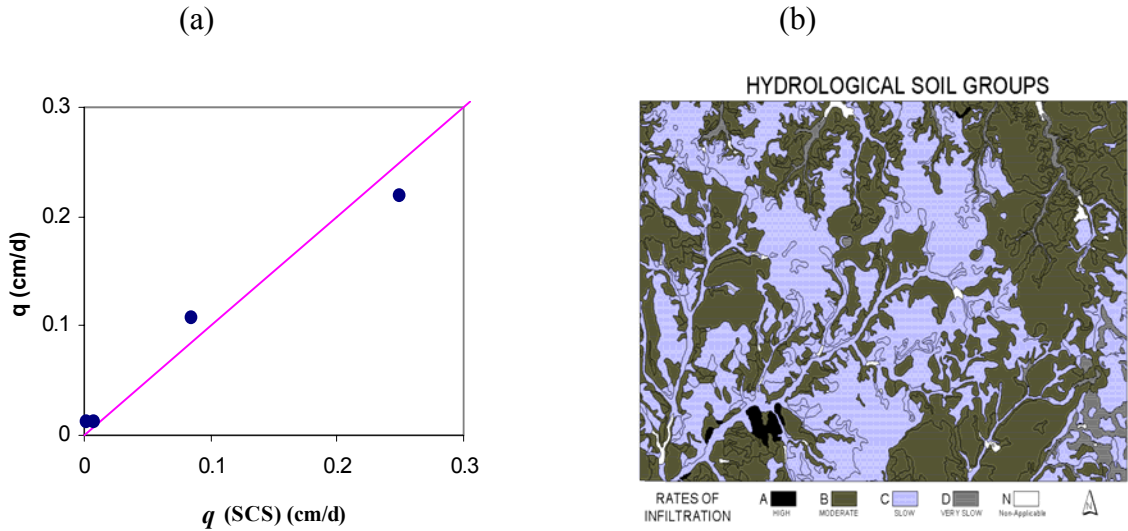


Fig.5. (a) Comparison between theoretical and SCS method ; (b) Hydrologic Soil Classification (Adapted from Hantush et al., 1999)

Comparison between Figs. 6(b) and 7(e) clearly shows that $\overline{C_g}$ values are highly underestimated on the basis of the SCS recharge. In fact, the spatial distribution of $\overline{C_g}$ (Fig. 6(b)) did not reflect the spatial pattern of the recharge distribution in Fig. 6(a), rather they showed almost uniformly low concentrations (less than 1 ppb) over the two watersheds. This is expected because of the longer residence time in the soil due to smaller SCS recharge estimates. Also, note that recharge estimates are averaged over the soil hydrologic class in the case of the SCS method, where as the conceptual recharge model (16) reflects the spatial variability of the soil type. And this, as well as the distribution of the depths to the water table, may have contributed to greater predicted mass emissions to the water table. Although the spatial distribution of the mean of dicamba concentrations in ground water (Fig. 7(e)) reflected

the same spatial pattern of the mean recharge $\bar{q}$ (Eq. 16), some of the low recharge areas however showed unexpectedly greater residual levels. This is a manifestation of the interactions among the physical and biochemical processes and spatial variability of the environmental factors, which affect the degradation of dicamba. Recall that the (apparent) residence time is not only a function of infiltration but also a function of the retardation factor. Remarkably, $\text{Var}(M_u)$ and $\text{Var}(C_g)$ displayed a different spatial pattern as shown in Figs. 7(d) and 7(f). This emphasizes the notion that the combined effect of spatial variability and uncertainty of the hydrologic and environmental factors, and not exclusively convection, is responsible for uncertainty in the predicted dicamba residuals. Although low variances of M_u and C_g were representative of the area in general, some portions, especially those surrounding the Morgan Creek showed greater variances. The coefficient of variation, however, remains high over the entire area.

CONCLUSIONS

A stochastically based methodology is presented for the assessment of groundwater vulnerability to nonpoint source pesticides in agricultural watersheds. A new relationship is presented for the estimation of seasonally averaged local recharge in terms of soil properties and seasonal average of depth to the water table. Application to a real case study showed a correlation between recharge estimates obtained by the theoretical equation with the net infiltration estimated on the basis of the SCS abstraction and Thornthwaite and Mather (1957) method. Physically based mass fraction models are also presented, which describe leaching of pesticides in the root zone and the intermediate vadose zone. The net effect of nonequilibrium transport on residual mass emissions is shown to be dependent on ratio of mass transfer coefficient and the first-order degradation rate in the immobile phase.

A stochastic framework is developed, using first order analysis, which describes uncertainty in the recharge and residual mass emissions of a given pesticide below the biologically active root zone. The framework was integrated with ArcView GIS and was applied to Mid-Atlantic coastal plain agricultural watersheds for the assessment of potential shallow groundwater contamination by the pesticide dicamba. Soil parameters and chemical and environmental parameters (e.g., half-life, organic carbon fraction, partition coefficient and others) are subject to uncertainty, thus, were modeled as random variables. And recharge and groundwater vulnerability to nonpoint source of dicamba was therefore evaluated under conditions of uncertainty. The models predicted significant mean residual levels of dicamba in ground water, which compared close to the HAL limit. The predicted mean values, however, should be viewed with uncertainty as the relatively large variances of the mean groundwater concentrations indicated. Results showed that the use of the SCS abstraction methods in groundwater pollution assessment may result in the underestimation of a potential pollution problem. The predicted mean and variance of dicamba concentrations in ground water are not exclusively driven by advective transport, rather, they reflect in their spatial distribution the complex interactions among the physical and biochemical processes, and related environmental factors.

The presented conceptual framework and the application to the Locust Grove study area clearly demonstrated the order of magnitude of expected uncertainty when fixed input parameters are considered in fate and transport models. Future attempts should account for uncertainty in NPS groundwater vulnerability assessments.

Notice: This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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Biography

Mohamed Hantush received his B. Sc. from Kuwait University in 1985, his MSc in 1988, and his PhD in 1993, all in Civil Engineering from the University of California at Davis. He worked as a Postdoctoral Researcher at the University of California at Davis. He is currently a Hydrologist at the U.S. EPA National Risk Management Research Laboratory. He is a member of ASCE, AGU, and NGWA.

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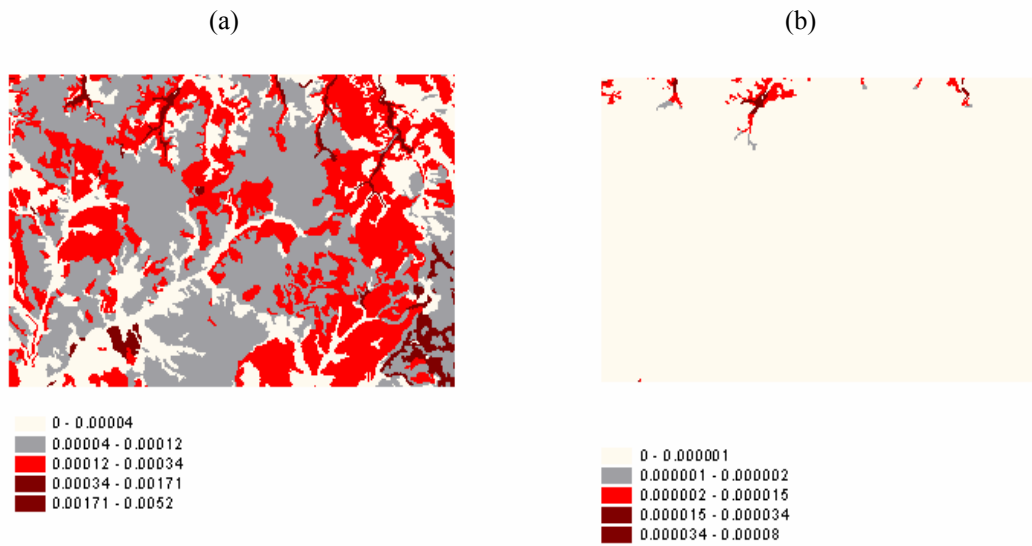


Fig. 6 (a) Recharge SCS (m/d); and (b) Mean groundwater $\overline{C_g}$ based on SCS recharge (Kg/m³)

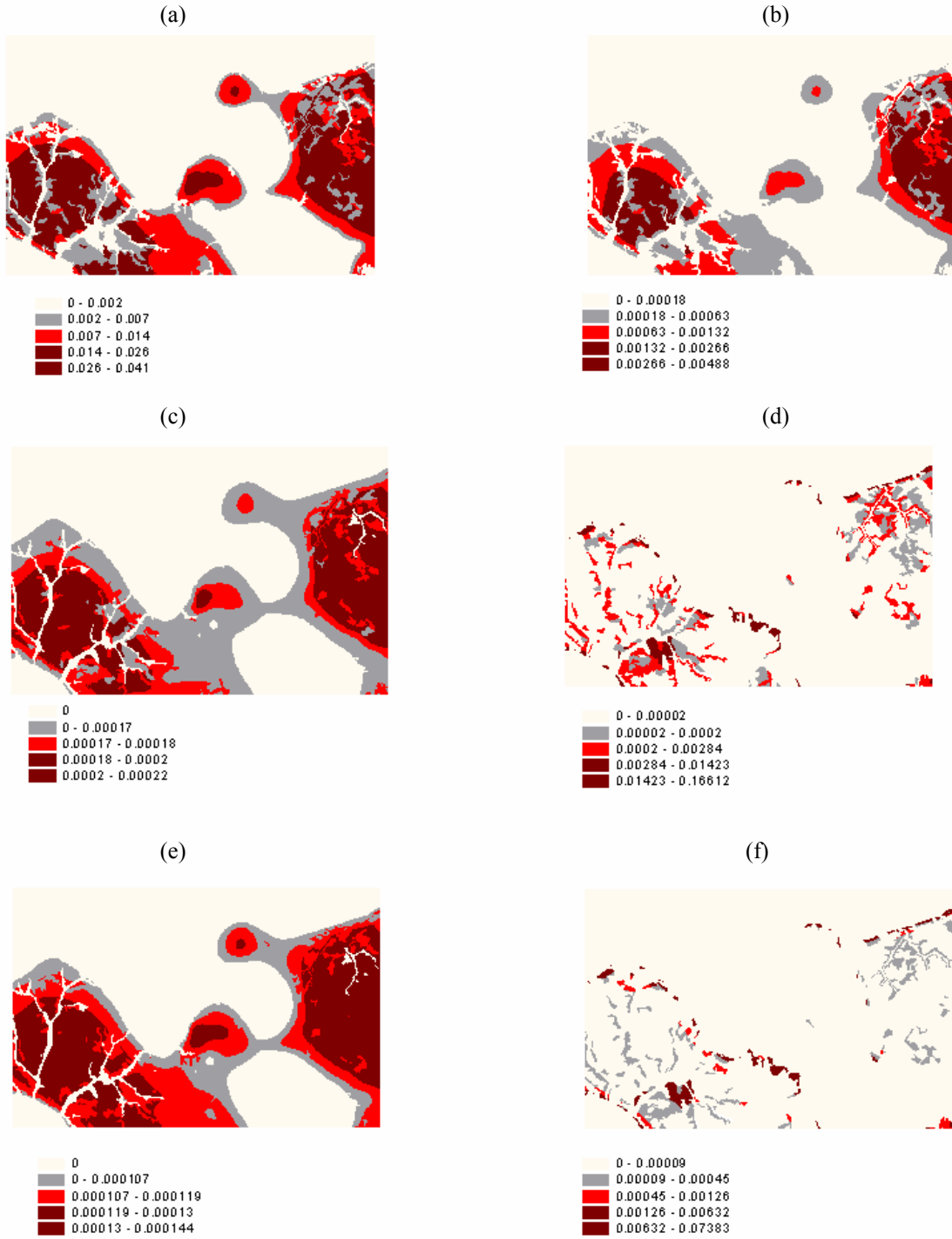


Fig. 7 ArcView display of (a) $\bar{q}$ (m/d) (Eq. 16); (b) $\text{Var } q$ (m^4/d^2); (c) $\overline{M_u}$ (Kg); (d) $\text{Var}(M_u)$ (Kg^2); (e) $\overline{C_g}$ (Kg/m^3); and (f) $\text{Var}(C_g)$ (Kg^2/m^6)

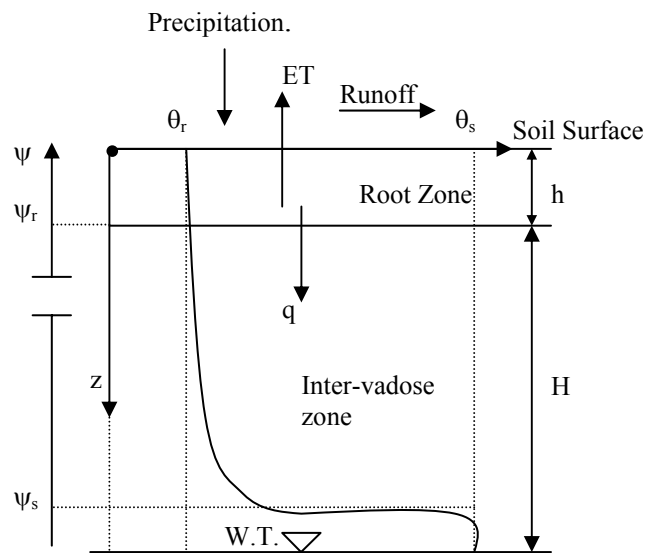


Fig. 1 Illustration of water balance in unsaturated zone.

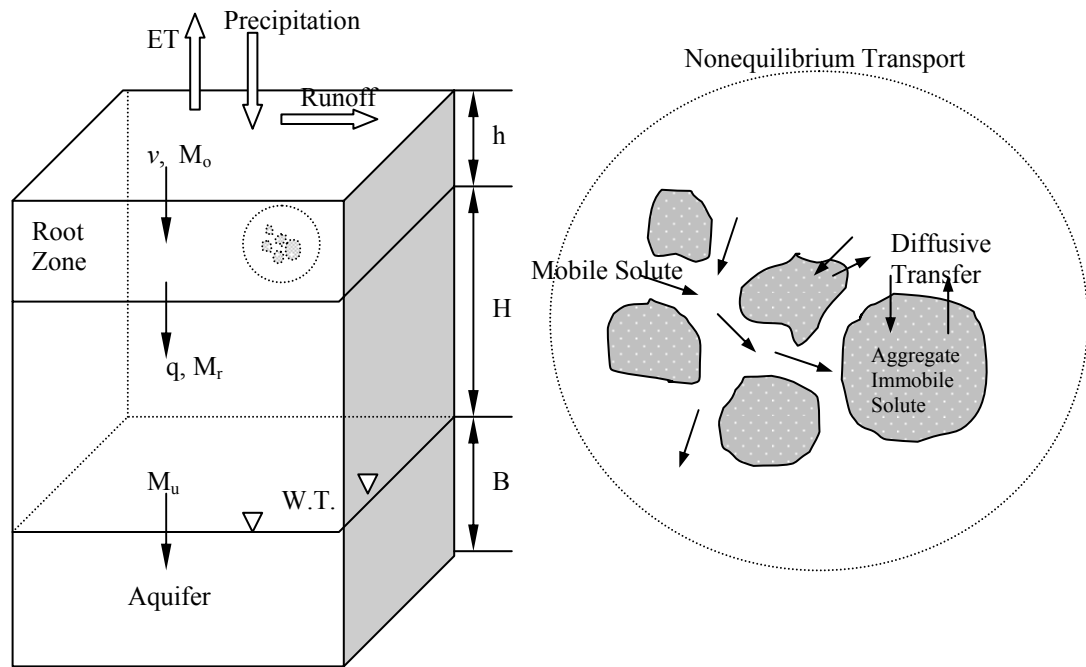


Fig. 2 (a) Illustration of a soil-aquifer system; and (b) fate and transport in mobile-immobile phase.

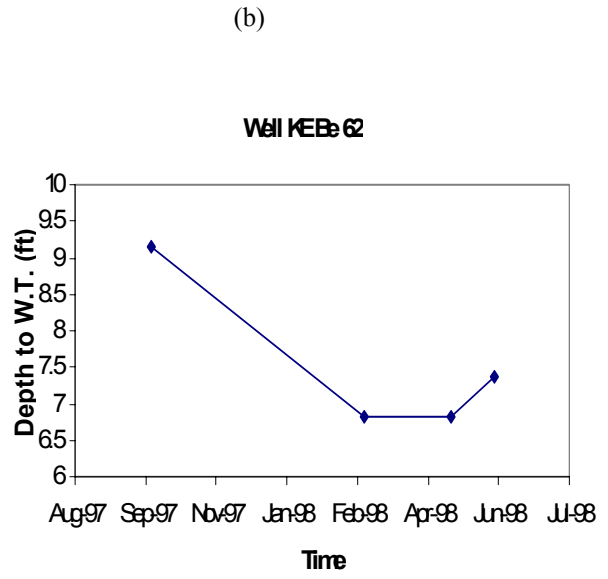
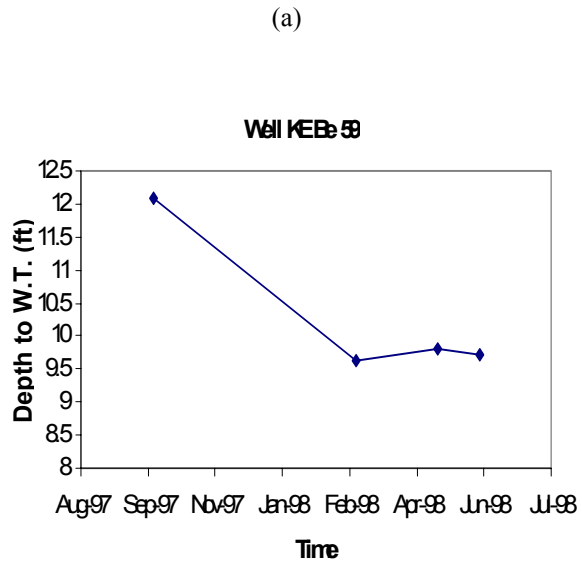


Fig.4 Records of Depth to water table in: (a) Well # KEBe59; and (b) Well #KEBe62

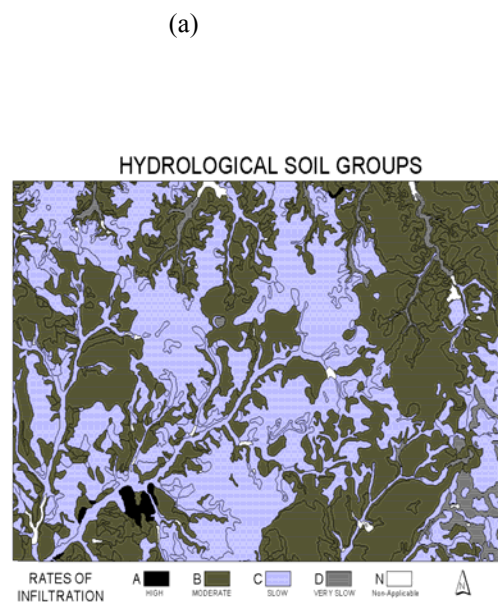
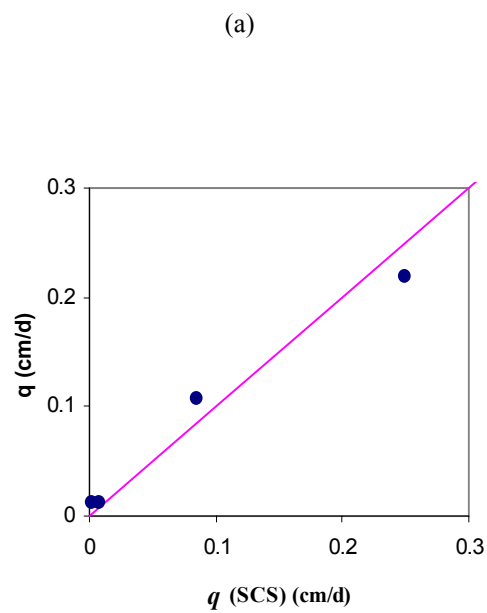


Fig.5. (a) Comparison between theoretical and SCS method ; (b) Hydrologic Soil Classification (Adapted from Hantush et al., 1999)