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An analytical model for the assessment of pesticide exposure levels in soils and groundwater

Mohamed M. Hantush and Miguel A. Mariño

Land, Air, and Water Resources, University of California, Davis, CA 95616, USA

E-mail: mmhantush@ucdavis.edu

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The movement and degradation of pesticide residues in soils and groundwater are complex processes affected by soil physical, (bio)chemical, and hydrogeological properties, climatic conditions, and agricultural practices. This work presents a physically-based analytical model suitable for long-term predictions of pesticide concentrations in groundwater. The primary interest is to investigate the impact of soil environment, related physical and (bio)chemical processes, especially, volatilization, crop uptake, and agricultural practices on long-term vulnerability of groundwater to contamination by pesticides. The soil is separated into root and intermediate vadose zones, each with uniform properties. Transport in each soil zone is modeled on the basis of complete mixing, by spatial averaging the related point multiphase-transport partial differential equation (i.e., linear-reservoir models). Transport in the aquifer, however, is modeled by a two-dimensional advection-dispersion transport equation, considering adsorption and first-order decay rate. Vaporization in the soil is accounted for by assuming liquid-vapor phase partitioning using Henry's law, and vapor flux (volatilization) from the soil surface is modeled by diffusion through an air boundary layer. Sorption of liquid-phase solutes by crops is described by a linear relationship which is valid for first-order (passive) crop uptake. The model is applied to five pesticides (atrazine, bromacil, chlordane, heptachlor, and lindane), and the potential for pesticide contamination of groundwater is investigated for sandy and clayey soils. Simulation results show that groundwater contamination can be substantially reduced for clayey soil environments, where bio(chemical) degradation and volatilization are most efficient as natural loss pathways for the pesticides. Also, uptake by crops can be a significant mechanism for attenuating exposure levels in groundwater, especially in a sandy soil environment, and for relatively persisting pesticides. Further, simulations indicate that changing agricultural practices can have a profound effect on vulnerability of groundwater to mobile and relatively persisting pesticides.

Keywords: Aquifers, contaminant transport, groundwater modeling, groundwater quality, solute transport and exchanges, water pollution, non-point source, pesticides, soil pollution, volatilization, crop-root uptake.

1 Introduction

Groundwater vulnerability to contamination has become an important environmental aspect of the use of pesticides in agriculture. In shallow and deep groundwater, a number of pesticides have been detected (e.g. [7]). Pesticides used for agricultural purposes are leached to the water table through deep percolation by infiltrating rainfall and return flow (excess to evapotranspiration) during irrigation. Vulnerability of groundwater to contamination by pesticides is a long-term process; it emphasizes the need for proper planning to prevent beforehand a contamination problem, or at best to circumvent further deterioration in groundwater quality. In order to evaluate the impact of a land-use decision policy on groundwater, it is neither feasible economically nor practical to conduct extensive and frequent field-scale monitoring of exposure levels of chemicals (i.e., concentrations) in groundwater. It may take decades before pesticides leaching from soils can reach and contaminate nearby drinking-water wells. Given the time frame limitation, a quick decision may be required by policy makers before approving a land-use practice, such as for agricultural purposes. Protection of groundwater quality benefits considerably from the ability to

predict exposure levels of chemicals in the subsurface environment, by using simulation models.

Physically-based transport models provide an efficient tool to predict exposure levels of contaminants in aquifers. In general, transport models vary from complex distributed parameters to simpler lumped-parameters linear-reservoir models. The former resemble more closely the actual physical system, e.g., heterogeneity, isotropy, etc., but are more difficult to solve than the latter; and they require a detailed set of data to warrant their use. Lumped-parameter models (or linear reservoir models) are easier to solve since they constitute linear systems and require less data (e.g. [12]); however, they are based on the restrictive assumption of complete mixing of the system variable, such as a solute mass. Duffy and Lee [9] demonstrated that outflow concentrations calculated on the basis of distributed-parameters and linear-reservoir models were similar, provided that the aquifer length is at least ten times its thickness.

Modeling transport of pesticides in soils is not a new undertaking. Jury et al. [14,15] developed a model for multiphase transport of trace organics in soils, and described volatilization by diffusive transfer of volatile pesticides through a stagnant air-boundary layer. Simplified models intended for ranking pesticide potential

for groundwater contamination were developed by Rao et al. [20] and Jury et al. [16]. The developed ranking indices considered linear, equilibrium liquid-vapor partition, linear, equilibrium adsorption, and (bio)chemical degradation. Boesten and Van der Linden [3] developed a numerical model for calculating nonvolatile pesticide residual levels in the plow layer, and leaching fractions to a shallow water table. In addition to first-order bio(chemical) degradation, they considered passive crop uptake as a potential loss pathway for the pesticides from the root zone. Jury and Gruber [17] developed a stochastic model for describing the probability distribution of residual mass fraction of a pesticide undergoing first-order degradation, under conditions of soil and climatic variability. Van der Zee and Boesten [22] incorporated the effect of spatial variability of adsorption, degradation, and soil thickness on the coefficient of variation of fraction of pesticide dose leached below 1 m depth. They considered first-order (passive) crop uptake in their analysis. Beltman et al. [2] composed an analytical model for transport of pesticides in the unsaturated and saturated zones. They coupled expressions developed by Jury and Gruber [17] and Van der Zee and Boesten [22], which describe fraction of pesticide dose that leaches from the heterogeneous unsaturated zone, to transport in groundwater. However, they ignored volatilization from soil surface, crop uptake, and dispersion in the aquifer.

The current work concerns analytical modeling and application to pesticide transport in soils and aquifers. The objectives are twofold. First, the development of an analytical simulation model, and second, its application to investigate the impact of crop uptake and volatilization on vulnerability of groundwater to contamination by pesticides under different soil environments and different agricultural practices. The soil is divided into a root zone and the intermediate vadose zone, in each of which complete mixing of the pesticide is assumed. The soil model takes into account processes such as leaching, adsorption, (bio)chemical degradation, crop-roots uptake, and volatilization. Linear, equilibrium liquid-vapor partition is considered based on Henry's Law, and linear, equilibrium adsorption is assumed for sorption and desorption in soil. A two-dimensional analytical solution for concentrations in groundwater is obtained from an elementary one (Bear [1, p. 273]), by integration in space and time. The solution considers leaching through soils, advection, dispersion, degradation, and linear equilibrium adsorption of pesticides in aquifers.

2 Solute transport equation

Three conceptual models are considered in the current study, each of which corresponds to a given zone: the root zone (upper soil), the intermediate-vadose zone (lower soil), and the saturated zone (aquifer). The migra-

tion pathway in soil is distinguished into two different zones because of the variability of soil texture and hydraulic properties, and the relative dominance of different physical, chemical, and biological processes for different zones. For example: (1) soil type may differ from one zone to another; (2) soil geometric and hydraulic properties differ for different zones; (3) average annual soil moisture content varies with depth; (4) most of the water loss due to evaporation, transpiration, and volatilization occurs in the root zone; and (5) water quality parameters such as soil distribution coefficients differ for soils with different fractions of organic carbon.

In the development of the lumped-parameters transport equations, we emphasize the continuity of the mass of a solute in the context of integrated mass balance of the multiphase solute transport in the root and intermediate vadose zones. The one-dimensional transport equation of a leaching solute existing in liquid, vapor, and adsorbed phases, and undergoing first-order decay, may be written as [14]:

$$\frac{\partial}{\partial t}(\kappa C_g + \theta C_l + \rho_b C_s) = \frac{\partial}{\partial z} \left(\kappa D_g \frac{\partial C_g}{\partial z} \right) + \frac{\partial}{\partial z} \left(\theta D_s \frac{\partial C_l}{\partial z} \right) - \nu \frac{\partial C_l}{\partial z} - r_s, \quad (1)$$

in which C_g is solute concentration in vapor phase (gram of chemical vapor/m³ of soil air), C_l is solute concentration in liquid phase (gram of solute/m³ of soil solution), C_s is adsorbed solute concentration (gram of sorbant/gram of dry soil), κ is volumetric air content, θ is volumetric water content, ρ_b is bulk soil density (gram/m³), D_g is the soil-gas diffusion coefficient (m²/day), D_s is porous media dispersion coefficient (m²/day), ν is convective soil moisture flux (m/day), t is time (days), z is soil depth (m), and r_s is the rate coefficient for transformation given by

$$r_s = k(\kappa C_g + \theta C_l + \rho_b C_s), \quad (2)$$

where k is the reaction rate constant (day⁻¹). Since we are concerned with the transport of the solute in the liquid phase, equation (1) is rewritten using phase partitioning relationships; the linear equilibrium sorption isotherm (liquid-sorbed concentrations) and the linear equilibrium liquid-vapor partitioning known as Henry's Law are expressed as

$$C_s = K_d C_l, \quad (3)$$

$$C_g = K_H C_l, \quad (4)$$

where K_d is the distribution coefficient and K_H is the dimensionless Henry's constant [18, p. 234], which can be calculated from the saturated vapor density C_g^* (g/m³) and solute solubility C_l^* (g/m³) [21],

$$K_H = C_g^*/C_l^*. \quad (5)$$

In terms of solute concentration in the liquid phase, C_l , equation (1) can be rewritten, after the use of (2)–(4), as

$$\theta R \frac{\partial C_l}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_e \frac{\partial C_l}{\partial z} \right) - \nu \frac{\partial C_l}{\partial z} - k\theta R C_l, \quad (6)$$

where D_e is the effective liquid-phase diffusion coefficient given by

$$D_e = (\kappa/\theta)K_H D_g + D_s \quad (7)$$

and R is a retardation factor given by

$$R = 1 + (\rho_b K_d + \kappa K_H)/\theta. \quad (8)$$

Equation (6) describes advection and dispersion of a reactive solute in the liquid phase. Note that from (7) and (8), the effect of volatilization is to increase the dispersion of the solute in water and to decrease its mobility by increasing the retardation factor.

3 Mass balance equations

In the next section we develop the integrated balance form of the transport equation (6) over each of the crop-root zones as well as the intermediate vadose zone. The simplifying assumptions are: (1) one-dimensional and steady-state downward percolation produced by seasonally-averaged irrigation demand and rainfall processes, both adjusted for possible losses due to evapotranspiration; (2) complete mixing in each zone; and (3) soil texture, hydraulic properties, and organic matter fraction are uniform within each zone; (4) linear equilibrium sorption isotherm; (5) diffusive solute-vapor movement occurs only in the crop-root zone, and losses from the soil surface to the atmosphere occur through an air boundary layer by vapor diffusion; and (6) passive root uptake.

3.1 Crop-root zone

The root zone or the soil-water zone extends from the ground surface down through the crop roots. Water in this zone exists at less than saturation except temporarily when excessive water reaches the ground surface as from rainfall or irrigation. Almost all of the water lost to evapotranspiration is accounted for in this zone. Leaching of solutes, such as pesticides, in this zone occurs during irrigation and rainfall activities where the infiltrating water mobilizes solute mass by advection downward to the water table. Volatilization and losses due to root uptake also occur in this zone.

3.1.1 Root uptake

For passive root uptake (see [3,4]), the rate of uptake of a solute by the crop, r_u , is described by

$$r_u = F S C_l, \quad (9)$$

in which F is the transpiration stream concentration factor, and S is the rate of water uptake by the crop (day^{-1}). Equation (6) modified for crop uptake can be written as

$$\theta R \frac{\partial C_l}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_e \frac{\partial C_l}{\partial z} \right) - \nu \frac{\partial C_l}{\partial z} - k_r C_l, \quad (10)$$

in which the effective loss rate k_r is given by

$$k_r = (k\theta R + FS). \quad (11)$$

Equation (10) describes advective-dispersive transport of a reactive solute subject to passive root uptake. Equation (11) describes the net degradation rate in the root zone due to the combined effect of (bio)chemical transformation and root uptake.

3.1.2 Volatilization from soil surface

Volatilization whereby chemicals vaporize and escape to the atmosphere may occur through a thin and stagnant layer of air above the soil surface. Following Jury et al. [14], vapor flux at the surface is assumed to diffuse through an air boundary layer of thickness d (m), before entering the atmosphere (figure 1a). Using Fick's Law, we may write the vapor-diffusive flux as

$$\kappa D_g \frac{\partial C_g}{\partial z} = \kappa D_g \frac{C_g(0, t) - C_g^a}{d}, \quad (12)$$

in which $C_g(0, t)$ is the vapor-phase solute concentration at the soil surface (g/m^3); and C_g^a is the concentration above the air boundary layer (g/m^3). For a well-mixed region of the atmosphere, $C_g^a = 0$, and we can rewrite (12) in terms of liquid solution concentrations using (4),

$$\kappa D_g K_H \frac{\partial C_l}{\partial z} = \sigma C_l(0, t), \quad (13)$$

where

$$\sigma = \kappa D_g K_H / d. \quad (14)$$

Equations (13) and (14) describe the net rate of loss of vapor concentration from the soil surface to the atmosphere through a thin boundary layer of air.

3.1.3 Integrated mass-balance equation

We start by integrating (10) over the depth of the roots h (figure 1a), from $z = 0$ to $z = h$,

$$\int_0^h \theta R \frac{\partial C_l}{\partial t} dz = \int_0^h \left(\frac{\partial}{\partial z} \left(\theta D_e \frac{\partial C_l}{\partial z} \right) - \nu \frac{\partial C_l}{\partial z} - k_r C_l \right) dz. \quad (15)$$

Realizing that the limits of integration are time invariant, and since properties are assumed uniform throughout the root zone, we can simplify (15) further,

$$\theta R \frac{d}{dt} \int_0^h C_l(z, t) dz = \left(\theta D_e \frac{\partial C_l(h, t)}{\partial z} - \nu^* C_l(h, t) \right) - \left(\theta D_e \frac{\partial C_l(0, t)}{\partial z} - \nu C_l(0, t) \right) - k_r \int_0^h C_l(z, t) dz, \quad (16)$$

where the net groundwater recharge, i.e., the water flux

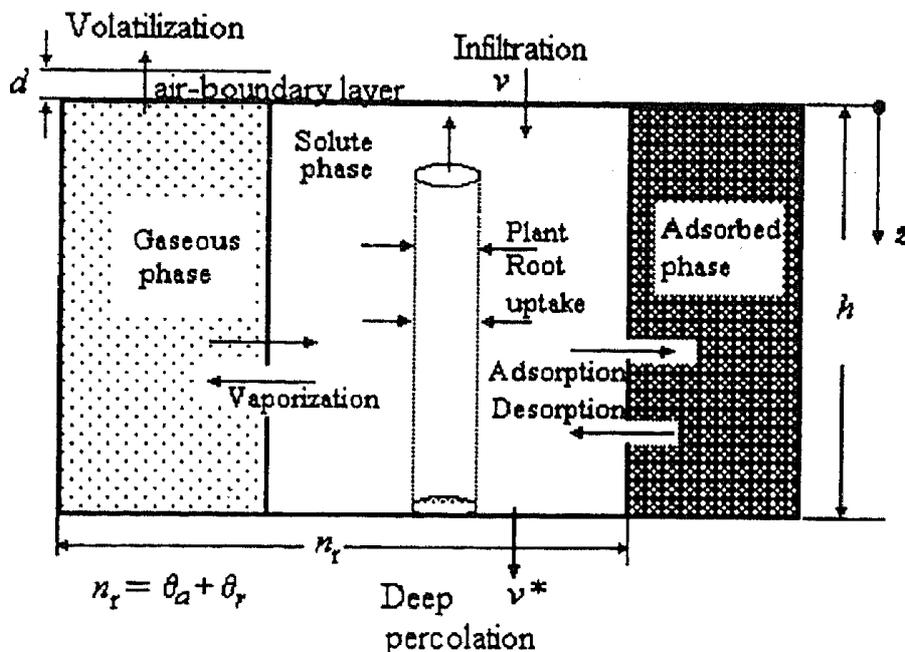


Figure 1a. Schematic representation of modeled processes in the root zone.

available for deep percolation below the root zone is given by

$$v^* = v - ET_c, \tag{17}$$

in which ET_c is the crop evapotranspiration rate (m/day). If we define the average solute concentration in the root zone, $C_r(t)$, as

$$C_r(t) = (1/h) \int_0^h C_l(z,t) dz, \tag{18}$$

then we may approximate (13) as follows:

$$\kappa D_g K_H \frac{\partial C_l}{\partial z} \approx \sigma C_r. \tag{19}$$

Furthermore, we approximate the solute mass flux at $z = h$ by the relation

$$\theta D_s \frac{\partial C_l(h,t)}{\partial z} - v^* C_l(h,t) \approx -v^* C_r, \tag{20}$$

which is widely used in mixing models (e.g. [8,12]). The approximation given by (20) is not valid in the most strict sense because it ignores the effect of dispersion. However, it is reasonable for shallow water tables, where the size of an application area is much greater than the depth to the water table, and where convection dominates over the dispersion mechanism. During precipitation and irrigation, we may write the flux boundary condition at the surface as

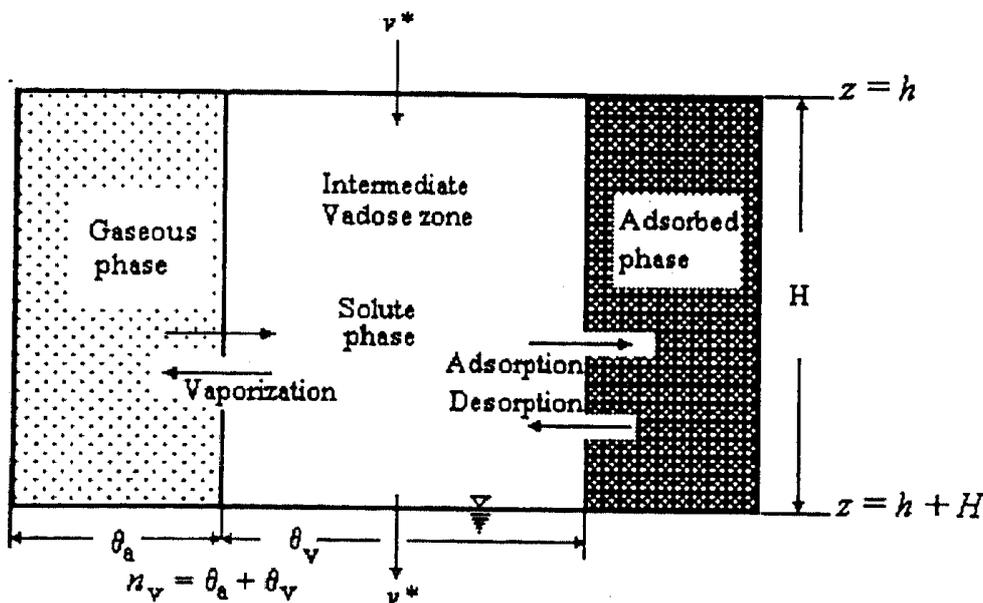


Figure 1b. Schematic representation of modeled processes in the intermediate vadose zone.

$$\theta D_s \frac{\partial C_l(0, t)}{\partial z} - \nu C_l(0, t) = -\nu C_0, \quad (21)$$

in which C_0 is the concentration of the chemical applied at the surface (g/m^3). We emphasize that (20) and (21) are understood as approximations intended for simplifying the analysis. Ignoring dispersion and heterogeneities may lead to serious underestimation of leaching below a given depth in soil (see, e.g., [2]). The substitution of (7) and (19)–(21) into (16) yields

$$\theta R h \frac{dC_r}{dt} = -\nu^* C_r + \nu C_0 - \sigma C_r - k_r h C_r, \quad (22)$$

which in turn can be written as

$$\frac{dC_r}{dt} + \beta_r C_r = \alpha_r C_0, \quad (23)$$

where

$$\beta_r = \frac{1 + (T_r/\lambda)(\ln(2) + \mu)}{T_r}, \quad (24)$$

$$\alpha_r = \nu / (h\theta_r R_r), \quad (25)$$

where

$$T_r = hR_r / (\nu^* / \theta_r), \quad (26)$$

$$\mu = (FS + \sigma/h)\lambda / (R_r \theta_r). \quad (27)$$

In (24), we substituted $\ln(2)/\lambda$ for the reaction rate constant k_r ; λ is the half-life (day); θ_r and R_r are the moisture content and retardation factors in the root zone, respectively. Note that R differs for different zones, because of the spatial variability of moisture content and the organic carbon fraction. Equation (23) is a first-order and linear differential equation that relates the averaged solute concentrations in the root zone to leaching, linear equilibrium adsorption, evapotranspiration, root uptake, first-order degradation, and volatilization. Although the concept of breakthrough time, which measures the mobility of a chemical, is not represented here due to the assumption of complete mixing, nevertheless, mobile chemicals have shorter residence times, T_r , and their averaged concentrations are less susceptible to the various loss pathways. This is consistent with equations (24) and (26), where the residence time T_r is greater for less mobile chemicals, hence, leading to greater losses by degradation, volatilization, and root uptake.

The solution of (7) is obtained using the integration factor:

$$C_r(t) = e^{-\beta_r(t-t_0)} C_r(t_0) + \int_{t_0}^t e^{-\beta_r(t-\tau)} \alpha_r C_0(\tau) d\tau. \quad (28)$$

Implicit in (28), the infiltrating flux ν , moisture content θ , and evapotranspiration ET_p are constant in the time interval $[t_0, t]$. Hence, for monthly/seasonal average input values, we can obtain closed-form solutions to (28) for the following specific cases.

(a) Uniform application at the surface, C_0

In this case, $C_0(\tau) = C_0$, and (28) reduces to

$$C_r(t) = e^{-\beta_r(t-t_0)} C_r(t_0) + \frac{\alpha_r}{\beta_r} C_0 (1 - e^{-\beta_r(t-t_0)}), \quad (29)$$

in which t_0 coincides with the beginning of a month/season and $t \in [t_0, t_1]$. The first term on the right-hand side represents the contribution of the solute background level in the root-soil profile, while the second term describes the contribution of the soil-surface source.

(b) Instantaneous application of a chemical mass

In this case, for a chemical mass M_0 , the solute mass flux per area (g/m^2) applied at the surface is related to the applied chemical mass M_0 , through the relationship

$$\nu C_0(\tau) = M_0 \delta(\tau - t_0), \quad (30)$$

in which $\delta(t)$ is the Dirac-delta function. In (30), it is assumed that M_0 is totally mobilized in the liquid phase, initially. If we substitute (30) into (28) and evaluate the integral, we obtain

$$C_r(t) = e^{-\beta_r(t-t_0)} C_r(t_0) + \frac{M_0}{\theta_r h R_r} e^{-\beta_r(t-t_0)}. \quad (31)$$

Equation (31) describes on an average basis the residual concentrations of an applied chemical mass at the soil surface and initially contaminated profile in the root zone.

3.2 Intermediate-vadose zone

The intermediate vadose zone extends from the bottom of the root zone to the water table. No loss of water to the atmosphere is expected from this zone. Almost all the water that enters this zone below the root zone percolates downward to the water table. Leachate concentration entering this zone is equal to the average concentration of the solute in the root zone. We integrate (6) over the intermediate-zone depth (figure 1b), from $z = h$ to $z = h + H$:

$$\int_h^{H+h} \theta R \frac{\partial C_l}{\partial t} dz = \int_h^{H+h} \left(\frac{\partial}{\partial z} \left(\theta D_e \frac{\partial C_l}{\partial z} \right) - \nu \frac{\partial C_l}{\partial z} - \theta k R C_l \right) dz. \quad (32)$$

The evaluation of (32) yields

$$\begin{aligned} & \theta R \frac{d}{dt} \int_h^{H+h} C_l(z, t) dz \\ &= \left(\theta D_e \frac{\partial C_l(H+h, t)}{\partial z} - \nu^* C_l(H+h, t) \right) \\ & \quad - \left(\theta D_e \frac{\partial C_l(h, t)}{\partial z} - \nu^* C_l(h, t) \right) \\ & \quad - \theta k R \int_h^{H+h} C_l(z, t) dz, \end{aligned} \quad (33)$$

in which θ , R , and k are assumed uniform. Similarly, if we define the average solute concentration in the intermediate-vadose zone C_u as

$$C_u(t) = (1/H) \int_h^{H+h} C_l(z, t) dz \quad (34)$$

and assume emission to the water table follows the boundary flux equation:

$$\theta D_s \frac{\partial C_l(H+h, t)}{\partial z} - \nu^* C_l(H+h, t) \approx -\nu^* C_u, \quad (35)$$

then, substituting (20), (34), and (35) into (33) yields

$$\theta R H \frac{dC_u}{dt} = -\nu^* C_u + \nu^* C_r - \theta k R H C_u. \quad (36)$$

In compact form, (36) is rewritten as

$$\frac{dC_u}{dt} + \beta_u C_u = \alpha_u C_r, \quad (37)$$

in which

$$\beta_u = \frac{1 + \ln(2)(T_u/\lambda)}{T_u}, \quad (38)$$

$$\alpha_u = 1/T_u, \quad (39)$$

where

$$T_u = H R_u / (\nu^* / \theta_u). \quad (40)$$

θ_u and R_u are the moisture content and retardation factor in the intermediate vadose zone, respectively. In arriving at (36), we have ignored diffusive flux of solute vapor from the intermediate vadose zone to the root zone ($\kappa D_g \partial / \partial z C_g(h, t) = \kappa D_g \partial / \partial z C_g(h+H, t) = 0$), which implies underestimation of vapor losses by volatilization. The volatilization rate from the soil surface increases, because the upward diffusive movement (Fick's Law) of solute vapor from the intermediate vadose zone tends to augment reduced vapor concentrations in the root zone.

Equation (37) is also a first-order and linear differential equation that relates the spatially-averaged solute concentration in the intermediate-vadose zone to leaching, first-order reaction, and linear equilibrium adsorption. The solution is given by

$$C_u(t) = C_u(t_0) e^{-\beta_u(t-t_0)} + \int_{t_0}^t e^{-\beta_u(t-\tau)} \alpha_u(\tau) C_r(\tau) d\tau. \quad (41)$$

Similarly, assuming monthly/seasonally-averaged leaching rate and moisture content, explicit forms can be obtained for the two cases discussed earlier.

(a) Uniform application at the surface, C_0

The substitution of (29) for $C_r(t)$ into (41) yields the following solution

$$C_u(t) = e^{-\beta_u(t-t_0)} C_u(t_0) + \frac{\alpha_u}{\beta_u - \beta_r} \left(C_r(t_0) - \frac{\alpha_r}{\beta_r} C_0 \right) \times e^{-\beta_u(t-t_0)} (e^{(\beta_u - \beta_r)(t-t_0)} - 1)$$

$$+ \frac{\alpha_r \alpha_u}{\beta_r \beta_u} C_0 (1 - e^{-\beta_u(t-t_0)}). \quad (42)$$

The first term on the right-hand side represents the contribution of the solute background level in the intermediate-vadose-soil profile, whereas the second term describes the contribution of solute emissions from the overlying crop-root zone.

(b) Instantaneous application of a chemical mass

In this case, we substitute (31) into (41), and the result is given by

$$C_u(t) = e^{-\beta_u(t-t_0)} C_u(t_0) + \alpha_u \left(C_r(t_0) + \frac{M_0}{\theta_r h R_r} \right) \times \frac{e^{-\beta_r(t-t_0)} - e^{-\beta_u(t-t_0)}}{\beta_u - \beta_r}. \quad (43)$$

In the next section we develop a two-dimensional groundwater transport model that considers the solute emissions to a water table, described by (42) and (43), as the primary source of contamination.

3.3 Solute transport in groundwater

In groundwater, the two-dimensional advection-dispersion of a reactive solute may be described by the following partial differential equation [1]

$$R \frac{\partial C}{\partial t} = D_{xx} \frac{\partial^2 C}{\partial x^2} + D_{yy} \frac{\partial^2 C}{\partial y^2} - u \frac{\partial C}{\partial x} - k_a C, \quad (44)$$

where C is the concentration of the contaminant in groundwater (g/m^3); D_{xx} is the hydrodynamic dispersion coefficient along the x axis (m^2/day), D_{yy} is the hydrodynamic dispersion coefficient along the y axis (m^2/day); and u is the average linear pore-water velocity along the x axis. D_{xx} and D_{yy} can be expressed in terms of two components [11]

$$D_{xx} = d^* + \alpha_L u, \quad (45)$$

$$D_{yy} = d^* + \alpha_T u, \quad (46)$$

in which d^* is the molecular diffusion coefficient multiplied by the tortuosity (m^2/day); α_L is the longitudinal dispersivity (m) along the mean flow direction; and α_T is the transverse dispersivity (m). Equation (44) can describe also advection-dispersion in a heterogeneous aquifer with a spatially variable hydraulic conductivity. In this case (44) is understood in a macroscopic sense, and the dispersion parameters in (45) and (46) are modified to account for macrodispersivities that are functions of the mean and variance of log conductivity, its integral scale, local dispersivities, the mean hydraulic gradient, and the mean specific discharge [13]. The use of constant macrodispersivities in (44) is only valid after large displacement of the contaminant plume where it has grown sufficiently in size which is greater than several integral scales of the log hydraulic conductivity field.

If we define

$$C^*(x, y, t) = e^{(k_a/R)t} C(x, y, t), \quad (47)$$

then (44) can be reduced to the following advection-dispersion and adsorption partial differential equation:

$$R \frac{\partial C^*}{\partial t} = D_{xx} \frac{\partial^2 C^*}{\partial x^2} + D_{yy} \frac{\partial^2 C^*}{\partial y^2} - u \frac{\partial C^*}{\partial x}, \quad (48)$$

in which

$$R = \left(1 + \frac{\rho_b k_d}{n} \right). \quad (49)$$

The solution of (48) in an infinite domain for an instantaneous injection of solute mass per depth, M , at time $t = 0$, and assuming zero initial concentration, $C(x, y, 0) = 0$, is given by [1]

$$C^*(x, y, t) = \frac{M}{4\pi\sqrt{D'_{xx}D'_{yy}t}} \times \exp\left\{-\left(\frac{(x-u't)^2}{4D'_{xx}t} + \frac{y^2}{4D'_{yy}t}\right)\right\}, \quad (50)$$

where $D'_{xx} = D_{xx}/R$, $D'_{yy} = D_{yy}/R$, $u' = u/R$, and $k'_a = k_a/R$. The solution of (44) for the instantaneous injection of solute mass M is obtained by substituting the elementary solution (50) into (47):

$$C(x, y, t) = \frac{M}{4\pi\sqrt{D'_{xx}D'_{yy}t}} \times \exp\left\{-\left(\frac{(x-u't)^2}{4D'_{xx}t} + \frac{y^2}{4D'_{yy}t} + k'_a t\right)\right\}. \quad (51)$$

The solute mass injected, per unit depth B of aquifer, from an incremental area $dA = d\xi d\eta$ (see figure 2) at the interface between the intermediate-vadose zone and the water table, during time interval $[\tau, \tau + d\tau]$ is

$$dM = \frac{\nu^*(\tau)}{nB} C_u(\tau) n d\xi d\eta d\tau, \quad (52)$$

and the corresponding increment of solute concentration is

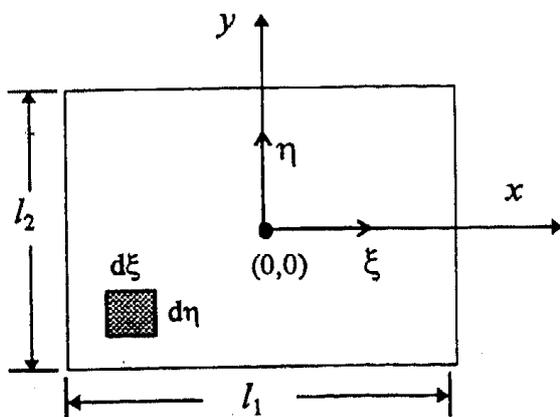


Figure 2. Schematic representation of application, related geometry, and hypothetical drinking water well.

$$dC(x, y, t) = \frac{\nu^*(\tau) C_u(\tau)}{4\pi B \sqrt{D'_{xx}D'_{yy}(t-\tau)}} \times \exp\left\{-\left(\frac{(x-u'(t-\tau))^2}{4D'_{xx}(t-\tau)} + \frac{y^2}{4D'_{yy}(t-\tau)} + k'_a(t-\tau)\right)\right\} d\xi d\eta d\tau, \quad (53)$$

in which $d\tau$ is understood to be infinitesimally small so that the solution (51), which is valid for instantaneous injection of solute mass dM , can be applied. For a non-point source, dM is not only a function of space (ξ, η) , but also a function of time, and its variation in time is the result of the dependence of the concentration in the intermediate-vadose zone on time, and the temporal variation of the leaching process below the root zone. If the pesticide is applied over an area of size $L_1 \times L_2$ (figure 3), then the solution of (44) can be obtained using the principle of superposition, i.e., integrating (53) over the application area (figure 2) and in time,

$$C(x, y, t) = \int_0^t \int_{-L_2/2}^{L_2/2} \int_{-L_1/2}^{L_1/2} \frac{\nu^*(\tau) C_u(\tau)}{B} \times \exp\left\{-\left(\frac{(x-\xi-u'(t-\tau))^2}{4D'_{xx}(t-\tau)} + \frac{(y-\eta)^2}{4D'_{yy}(t-\tau)} + k'_a(t-\tau)\right)\right\} / (4\pi\sqrt{D'_{xx}D'_{yy}(t-\tau)}) d\xi d\eta d\tau. \quad (54)$$

Since the terms that contain the dummy variables ξ and η are separable, (54) can be written as

$$C(x, y, t) = \int_0^t \frac{\nu^*(\tau) C_u(\tau)}{4\pi B \sqrt{D'_{xx}D'_{yy}(t-\tau)}} e^{-(k'_a)(t-\tau)} \times \left\{ \int_{-l_1/2}^{l_1/2} \exp\left\{-\frac{(x-\xi-u'(t-\tau))^2}{4D'_{xx}(t-\tau)}\right\} d\xi \times \int_{-l_2/2}^{l_2/2} \exp\left\{-\frac{(y-\eta)^2}{4D'_{yy}(t-\tau)}\right\} d\eta \right\} d\tau. \quad (55)$$

Upon the use of the transformations $\xi^* = [\xi - (x - u'(t - \tau))] / (2[D'_{xx}(t - \tau)]^{1/2})$ and $\eta^* = (\eta - y) / (2[D'_{yy}(t - \tau)]^{1/2})$, the integrals with respect to ξ and η can be evaluated to yield

$$C(x, y, t) = (1/B) \int_0^t \nu^*(\tau) C_u(\tau) e^{-(k'_a)(t-\tau)} \times G(\tau; x, t) F(\tau; y, t) d\tau, \quad (56)$$

in which

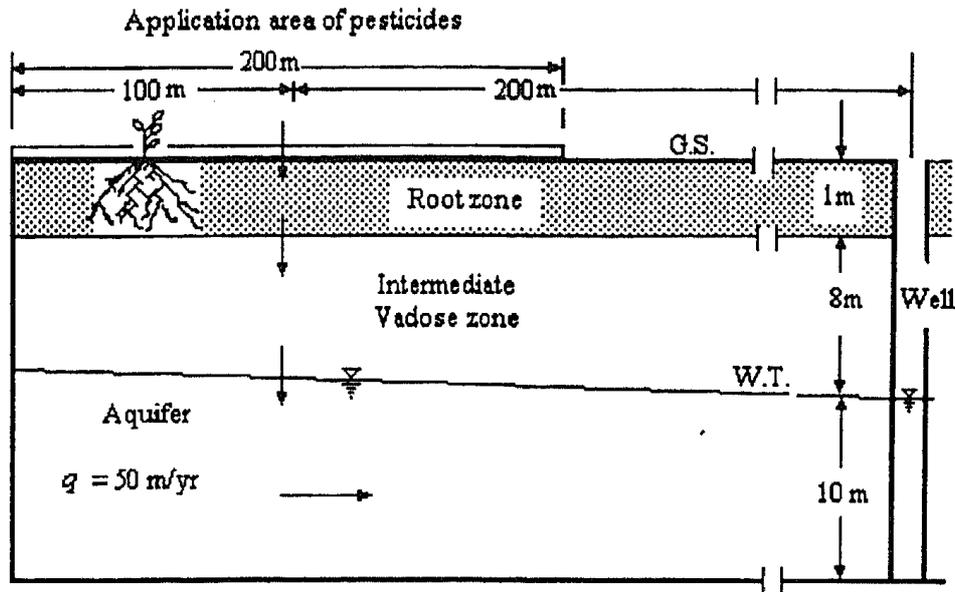


Figure 3. Schematic representation of the soil-aquifer system with related geometry used in the simulations.

$$\begin{aligned}
 G(\tau; x, t) &= \frac{1}{2} \operatorname{erf} \left(\frac{l_1/2 + |x - u'(t - \tau)|}{2\sqrt{D'_{xx}(t - \tau)}} \right) \\
 &\quad - \frac{1}{2} \operatorname{erf} \left(\frac{-l_1/2 + |x - u'(t - \tau)|}{2\sqrt{D'_{xx}(t - \tau)}} \right), \\
 &\quad \text{if } |x - u'(t - \tau)| > l_1/2, \\
 &= \frac{1}{2} \operatorname{erf} \left(\frac{l_1/2 - (x - u'(t - \tau))}{2\sqrt{D'_{xx}(t - \tau)}} \right) \\
 &\quad + \frac{1}{2} \operatorname{erf} \left(\frac{l_1/2 + (x - u'(t - \tau))}{2\sqrt{D'_{xx}(t - \tau)}} \right), \\
 &\quad \text{if } |x - u'(t - \tau)| \leq l_1/2, \quad (57)
 \end{aligned}$$

and

$$\begin{aligned}
 F(\tau; y, t) &= \frac{1}{2} \operatorname{erf} \left(\frac{l_2/2 + |y|}{2\sqrt{D'_{yy}(t - \tau)}} \right) \\
 &\quad - \frac{1}{2} \operatorname{erf} \left(\frac{-l_2/2 + |y|}{2\sqrt{D'_{yy}(t - \tau)}} \right), \\
 &\quad \text{if } |y| > l_2/2, \\
 &= \frac{1}{2} \operatorname{erf} \left(\frac{l_2/2 - y}{2\sqrt{D'_{yy}(t - \tau)}} \right) \\
 &\quad + \frac{1}{2} \operatorname{erf} \left(\frac{l_2/2 + y}{2\sqrt{D'_{yy}(t - \tau)}} \right), \\
 &\quad \text{if } |y| \leq l_2/2. \quad (58)
 \end{aligned}$$

Equations (56)–(58) describe analytically the mobility, transformation, and spreading characteristics of the

residual mass of a chemical in groundwater, after leaching through the soil.

For the monthly/seasonal variations of input variables such as moisture content, groundwater recharge, evapotranspiration, application of, e.g., pesticides and herbicides, and volatilization, (56) can be written on a monthly/seasonal basis as

$$\begin{aligned}
 C(x, y, t) &= (1/B) \sum_{s=1}^N \nu_s^* \int_{t_{s-1}}^{t_s} C_u(\tau) e^{-k_d(t-\tau)} \\
 &\quad \times G(\tau; x, t) F(\tau; y, t) d\tau, \quad (59)
 \end{aligned}$$

where $t_N = t$.

4 Application

Table 1 shows selected chemical properties of the pesticides atrazine, chlordane, heptachlor, bromacil, and lindane. By comparing the values of the chemical organic C partition coefficient, degradation half-lives, and the dimensionless Henry's constant (table 1), it is clear that the five selected pesticides differ significantly with

Table 1
Organic C partition coefficients, degradation half-lives, and Henry's constants for five pesticides.

Pesticide	K_{oc} (cm^3/g)	$t_{1/2}$ (days)	K_H
Atrazine*	160	71	2.5×10^{-7}
Chlordane*	38000	3500	2.2×10^{-4}
Heptachlor*	24000	2000	1.45×10^{-1}
Bromacil*	72	350	3.7×10^{-8}
Lindane*	1300	266	1.3×10^{-4}

Source: Jury et al. [15] and Rao et al. [20].

* Application rate is 3.4 kg/ha, applied once a year at the beginning of the growing season.

Table 2
Typical values of properties for sandy and clayey soils.

Property	Sandy soil	Clayey soil
Bulk density g/cm ³	1.7	1.5
Average water constant	0.22	0.35
Residual water content *	0.045	0.07
Organic C fraction	0.005	0.03
Porosity	0.4	0.5

* Residual water content is used for the root zone during the growing season (May–Sep).

respect to their mobility dictated by the organic C partition coefficient, persistence which is a function of degradation half-life, and volatilization, whereby a chemical evaporates and escapes from the soil surface, which depends on the value of K_H . For example, atrazine is expected to be highly mobile with very low persistence in the soil, because of its relatively low organic C partition coefficient and low half-life. The application area is assumed to be 200 m × 200 m (4 ha) and the application rate for each pesticide is assumed to be 3.4 kg/ha (assumed a worst case scenario by Varshney et al. [23]), once a year at the beginning of the growing season of the crop, e.g., maize. Two growing scenarios are considered, (May 1–September 30) and (March 1–July 31). Two types of soils are investigated, sand and clay. They differ significantly with respect to their vulnerability to groundwater contamination (e.g. [17]), and typical values for their properties are displayed in table 2. Table 3 shows geometric and geohydrologic data used for the simulations. Organic carbon fraction is neglected in the intermediate vadose zone and in the aquifer, hence, mobility of a pesticide is only affected in the root zone because of retardation there. The aquifer is assumed to be of alluvial origin and characterized, predominantly, by sand and gravel layers. The average depth of the root zone is assumed to be 1 m, which is typical to corn crops. The climatic data with respect to averaged precipitation and reference evapotranspiration is typical to the Sacramento Valley in California (see table 4). For calculating the rate of water uptake by the crop, S , we use the relationship suggested by Boesten and van der Linden [3],

Table 3
Geohydrologic data.

Property	Value
Thickness of root zone (m)	1
Thickness of intermediate-vadose zone (m)	8
Thickness of aquifer (m)	10
Groundwater Darcian velocity (m/yr)	50
Longitudinal dispersivity (m)	5
Transverse dispersivity (m)	0.1
Effective molecular diffusion (cm ² /sec)	10 ⁻⁵
Gaseous diffusion coefficient (cm ² /day)	4320 *
Air-boundary layer thickness (cm)	5 *

* Suggested by Jury et al. [14].

Table 4
Meteorological and crop data.

Property	Value
Average precipitation (m) (May–Sep.) ¹	0.0216
Average precipitation (m) (Mar.–Jul.) ¹	0.102
Average precipitation (m) (Oct.–Apr.) ¹	0.4
Average precipitation (m) (Aug.–Feb.) ¹	0.32
Average potential ET (m) (May–Sep.) ²	0.885
Average potential ET (m) (Mar.–Jul.) ²	0.765
Average surface runoff (m) (May–Sep.) ³	0
Average surface runoff (m) (Mar.–Jul.) ⁴	0.038 m (clay) 0.024 m (sand)
Average surface runoff (m) (Oct.–Apr.) ⁴	0.15 m (sand) 0.22 m (clay)
Average surface runoff (m) (Aug.–Feb.) ⁴	0.13 m (sand)
Reduction factor (γ)	0, 0.5, 0.8
Average leaf area index (cm ² /cm ²) (maize crop) ⁵	2.4
Transpiration stream concentration factor ⁵	1

¹ Average values in Davis based on (1917–1972) recorded data [5].

² Based on average values for reference ET in Davis [19].

³ Assumed.

⁴ Calculated using the SCS method, assuming normal antecedent moisture conditions.

⁵ Adapted from Boesten and van der Linden [3], averaged over the growing season.

$$S(\gamma/h)ET_p(1 - e^{-0.6I}), \quad (60)$$

in which γ is a reduction factor assumed here a constant; ET_p is the potential ET ; and I is the leaf area index (cm²cm⁻²). In a more realistic manner, Feddes et al. [10] considered the variation of the reduction factor γ as a function of matric suction, for modeling the effect of root uptake on moisture distribution in soil. In the simulations (figures 4–7), we ignore the fraction of deep percolation (below the root zone) produced by water in excess to irrigation demand. That is, future predictions are based on irrigation rates that meet estimated crop evapotranspiration ET_c (see [19]). Predictions for the pesticide levels in groundwater are made at a hypothetical drinking water well located at a distance 200 m down gradient from the center of the application area ($x = 200$ m, $y = 0$ m). Figure 3 shows a schematic representation of the soil-aquifer system with related geometry used in the simulations. Simulated groundwater concentrations shown in figures 4–7 correspond to the agricultural practice: a growing season (May–September) of duration of 153 days (0.42 yr) with average precipitation of 0.0216 m/153 days, and a wet season (October–April) of duration 212 days (0.58 yr) with average precipitation of 0.4 m/212 days. Emissions of pesticides to groundwater predominantly occur during the wet season, where leaching below the root zone is most significant due to greater than the annual average of the precipitation.

The results displayed in figures 4–8 are based on instantaneous injection of the given pesticide mass at the beginning of the growing season. Thus, we use equations

(31), (43), and (59), in which the integral is evaluated using the Romberg method. For efficient numerical evaluation of the integral, we note that, for a fixed x and t , the function $G(\tau; x, t)$ behaves as a finite pulse contained in the interval $[a_1(t), b_1(t)]$, where

$$a_1(t) = t - [(x + l_1/2)/u'] - (4/u')\sqrt{D'_x t},$$

and

$$b_1(t) = t - [(x - l_1/2)/u'] + (4/u')\sqrt{D'_x t}.$$

Therefore, rather than integrating from t_{s-1} to t_s in (59), we instead integrate from $\max[t_{s-1}, a_1(t)]$ to $\min[t_s, b_1(t)]$. Note that for large x and small t , evaluating the integral is redundant and $b_1(t)$ can be negative, implying that the contaminant pulse is yet to arrive at x and the concentration is zero there.

5 Discussion

5.1 Effect of crop uptake

Figure 4 shows predicted atrazine concentrations for sandy and clayey soils, assuming agricultural practices are maintained throughout the prediction period. For both soils, the predicted atrazine concentrations at the drinking water well showed very low exposure levels (in ppb) and rather a strong stationary-periodic behavior

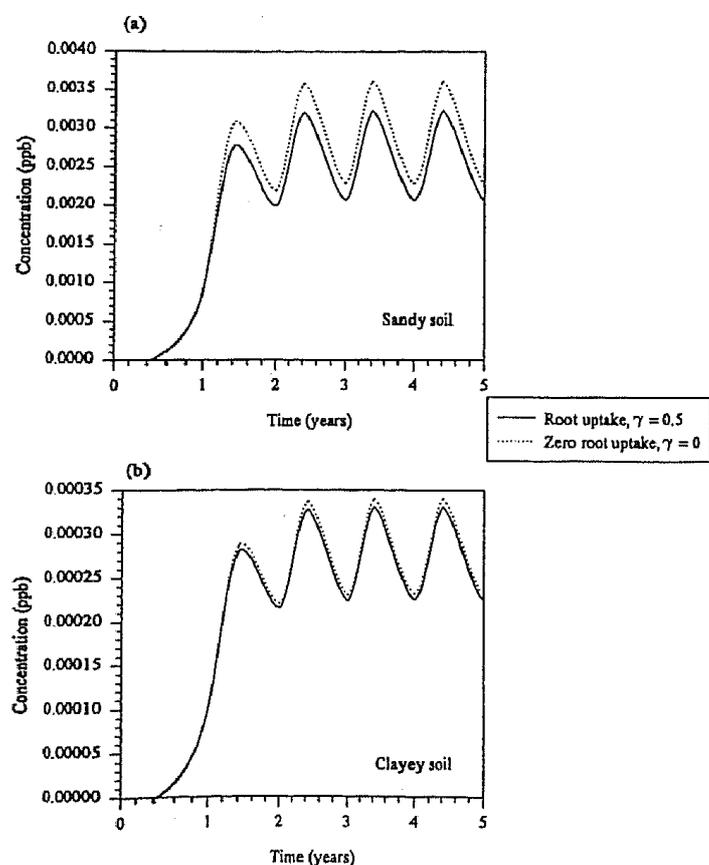


Figure 4. Predicted exposure levels of atrazine (ppb) in the hypothetical drinking water well for $\gamma = 0$ and 0.5: (a) sandy soil, and (b) clayey soil.

(unsteady in the regular sense) after two years. Such behavior represents the kind of temporal variability which is a manifestation of the combined effect of high degradation rate of atrazine and the seasonal effect of the leaching mechanism produced by the net infiltration below the root zone. Transport through a clayey soil resulted in much lower atrazine concentrations, by an order of magnitude (figure 4b), when compared to exposure levels predicted on the basis of a sandy soil (figure 4a). The greater the organic carbon fraction, the greater the retardation atrazine encounters due to adsorption in the root zone, whereas increasing the retardation results in relatively greater residence time, T_r , i.e., holding up the pesticide for a longer time in the root zone. Because such a condition favors relatively greater losses of adsorbate by degradation, the net result is concentrations being emitted to the water table via a clayey soil shows much smaller predicted exposure levels in the well (figure 4a), when compared to the case when emissions to the water table occur through a sandy soil (figure 4b). It is imperative in this effort to realize that in addition to degradation, persistence of pesticides in the soil may be significantly reduced due to volatilization and crop-root uptake, especially for longer residence time such as in a clayey soil (also, refer to equations (24), (26) and (27)). However, for less volatile pesticides like atrazine ($K_H = 2.5 \times 10^{-7}$), low exposure levels in groundwater are a manifestation of low persistence due to bio(chemical) degradation, rather than volatilization and root uptake. Low concentrations of atrazine in the root zone, due to degradation, result in reduced passive uptake by crops, because of the linear dependence of the latter on the soluble concentrations, as equation (9) indicates. As mentioned earlier, the strong temporal variability of atrazine residual levels in groundwater, albeit being periodic because of the seasonally-averaged climatic input data (recall, two seasons are considered here), is attributed to the combined effect of high degradation rate and seasonal variations of the leaching process. The effect of soil type on leaching is accounted for in this effort, indirectly, by allowing for surface runoff calculated by the SCS method (see, e.g., [6, p. 147]). Such an approximation is somewhat stringent, however, intended for distinguishing the relative behavior of a given pesticide in different soil environments, rather than predicting absolutely the effect of hydraulic properties of the soil on the prediction process. Nevertheless, a lower infiltration rate in a clayey soil, as indicated by greater estimate of surface runoff (table 4), results in lower persistence of atrazine in the root zone, because of greater residence time and reduced residual concentrations due to greater degradation. Subsequently, the effect of crop-root uptake on the predicted concentrations in groundwater is marginalized (figure 4b), whereas figure 4a shows in rather a more resolute manner the sensitivity of predicted atrazine concentrations with respect to crop uptake, when the soil environment is

predominantly sand. Prediction based on $\gamma = 0.5$ shows reductions in atrazine levels as large as 12.5% if root uptake is taken into consideration as a viable loss pathway from a sandy soil.

Figure 5 shows predicted exposure levels of bromacil in the drinking well for the two cases of sandy and clayey soils. Because of the low organic C partition coefficient and relatively large half-life of the pesticide bromacil (table 1), it is highly mobile and somewhat persistent in soils and, furthermore, nonvolatile due to its negligibly small dimensionless Henry's constant ($K_H = 3.7 \times 10^{-8}$). Altogether, these characteristics favor greater residual concentrations in the root zone, hence, rendering bromacil a good candidate among the selected pesticides to provide a greater insight into the effect of crop uptake, ultimately, on the predicted concentrations in groundwater. In contrast to the behavior of atrazine, predicted bromacil concentrations in groundwater show a gradual buildup toward steady-state periodic levels that are greater by two orders of magnitude, after 10 years from the beginning of the agricultural practices. It is clear that in a sandy soil environment the cumulative effect of root uptake has a profound effect on the predicted bromacil levels in the drinking water well, after approximately 3 years (figure 5b). For $\gamma = 0.5$ and 0.8, the predicted steady-state concentrations are 38% and 50%, respectively, smaller than the values predicted when crop uptake is

not accounted for. In the case of a clayey soil, the predicted concentrations are smaller by an order of magnitude than in the case of a sandy soil, and the effect of crop uptake is relatively less remarkable with concentrations reduced by as much as 13% and 18% for $\gamma = 0.5$ and 0.8, respectively (figure 5a).

5.2 Effect of volatilization

Heptachlor is much less mobile and slowly degradable when compared to atrazine and bromacil, because of its greater organic C partition coefficient (greater retardation) and greater half-life; however, it is highly volatile due to its high dimensionless Henry's number ($K_H = 0.145$). Figure 6 shows predicted heptachlor concentrations for sandy and clayey soil environments. In both soils, predicted exposure levels in the hypothetical drinking well show a continuous buildup toward steady levels, with the temporal variability being smothered by the high persistence and buildup of the concentrations. Due to the reduced leaching capacity and greater retardation, the longer residence time in a clayey soil favors greater losses by volatilization, subsequently, much smaller exposure levels of the highly volatile heptachlor in groundwater, by less than half the levels predicted on the basis of a sandy soil. Further, the estimated concen-

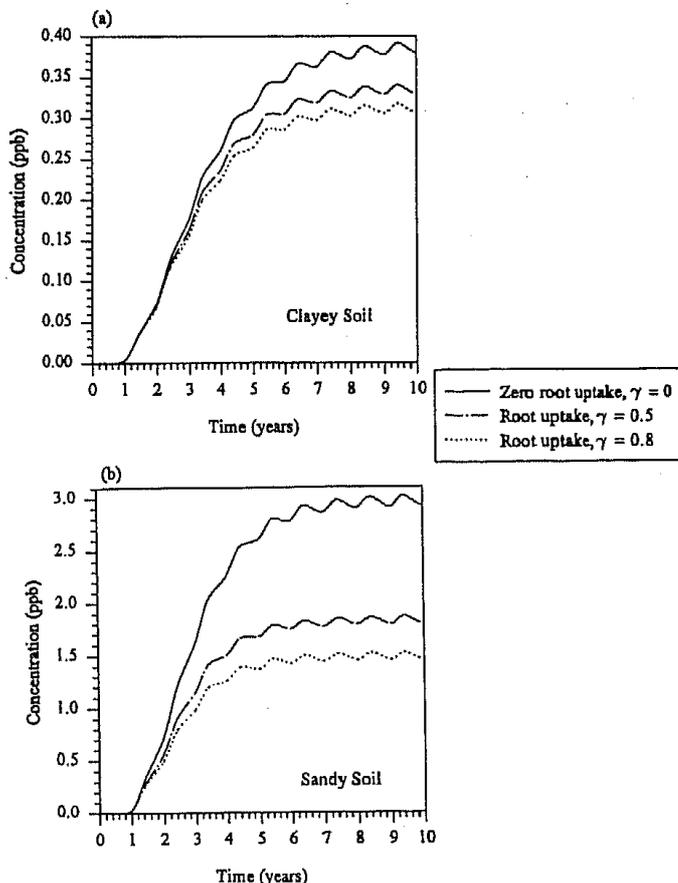


Figure 5. Effect of crop uptake on predicted exposure levels (ppb) of bromacil in the hypothetical drinking water well: (a) clayey soil, and (b) sandy soil.

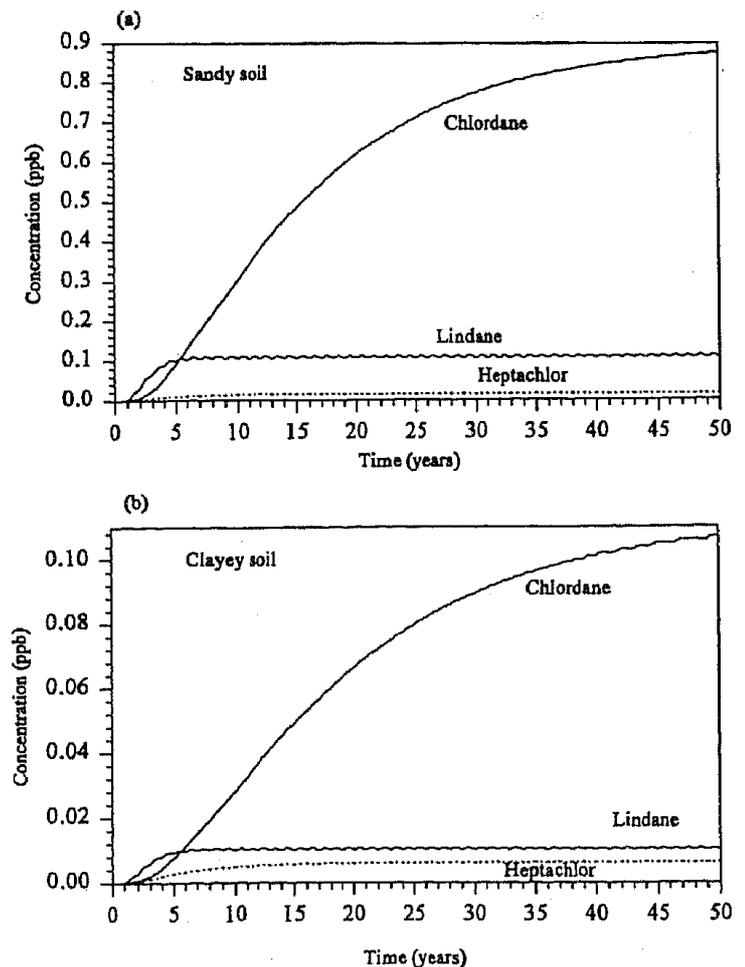


Figure 6. Predicted exposure levels (ppb) of heptachlor (sandy and clayey soils) and lindane (clayey soil), in the drinking water well.

trations in figure 6 show no sensitivity with respect to root uptake, even for the extreme case of $\gamma = 1$. This is a direct consequence of losses by volatilization which lead to lower concentrations, hence, negligible passive root uptake.

Notwithstanding the relative similarity between heptachlor and chlordane with respect to mobility and degradation, heptachlor shows much smaller predicted concentrations in groundwater due to its greater susceptibility to volatilization than chlordane, as shown in figure 7. The relatively nonvolatile lindane shows predicted concentrations greater than chlordane up to 5 years, before leveling off, but with a temporally variable pattern, because of the relatively low persistence of the latter in soils (i.e., greater degradation). It is worth emphasizing that increased losses by volatilization due to upward movement of water which is instigated by evaporation from the soil surface, is not modeled here, especially in an inactive (nongrowing) season characterized by drier climate. Because of the upward movement of water, solute accumulates at the interface between the soil surface and the air boundary layer, thus leading to an increased volatilization rate even for pesticides with low K_H , such as atrazine and bromacil [15].

An interesting feature in figure 6 is the resemblance, up to year five, between the estimated concentrations in groundwater, of lindane, based on clayey soil, and heptachlor, however, based on sandy soil. This indicates how similar the behavior of different pesticides in groundwater can be under different soil environments. Also, pesticides with relatively short half-life, such as atrazine, lindane, and bromacil show a less variable

transient buildup in concentrations (i.e., prior to steady state), which is overwhelmed by the effect of annually-averaged climatic data. However, they approach a steady but temporally variable pattern which is dominated by seasonal effects, albeit the anticipated smoothing effect of macrodispersion ($\alpha_L = 5$ m).

5.3 Effect of agricultural practices

The impact of agricultural practices on groundwater quality is investigated in two ways. First, the integration demand is adjusted for precipitation, and second, by considering an alternative growing season which starts two months earlier, March 1, and lasts throughout the month of July (i.e., until July 31). Note that results of figures 4–7 are based on the practices that irrigation water so applied meets crop evapotranspiration, and that the growing season is from May 1 to September 30. Only here, we have adjusted irrigation demand to meet the deficit of seasonally-averaged precipitation from seasonally-averaged crop evapotranspiration. Figure 8 shows the predicted concentrations of bromacil in groundwater, for the first growing season (May 1–September 30) and the alternative growing season (March 1–July 31), and for sandy soil. Comparison between figures 8 and 5b (growing season May 1–September 30) shows that the reduced leaching potential below the root zone (deep percolation), by adjusting irrigation for precipitation, results in substantial reduction of predicted bromacil concentrations. Also, under similar climatic conditions, starting the growing season two months earlier, resulted in a less rapid buildup and considerable reduction of long-term exposure levels in

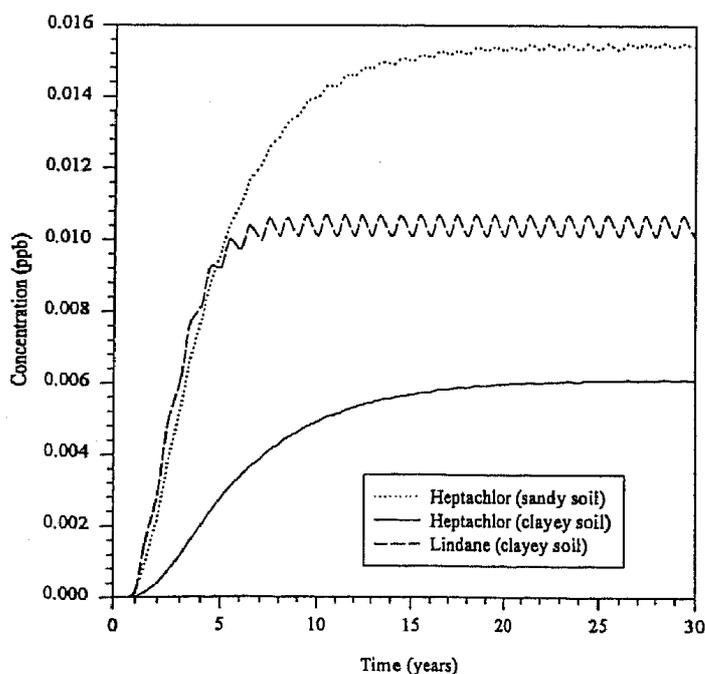


Figure 7. Predicted exposure levels (ppb) of chlordane, lindane, and heptachlor in (ppb) in the drinking water well: (a) sandy soil, and (b) clayey soil.

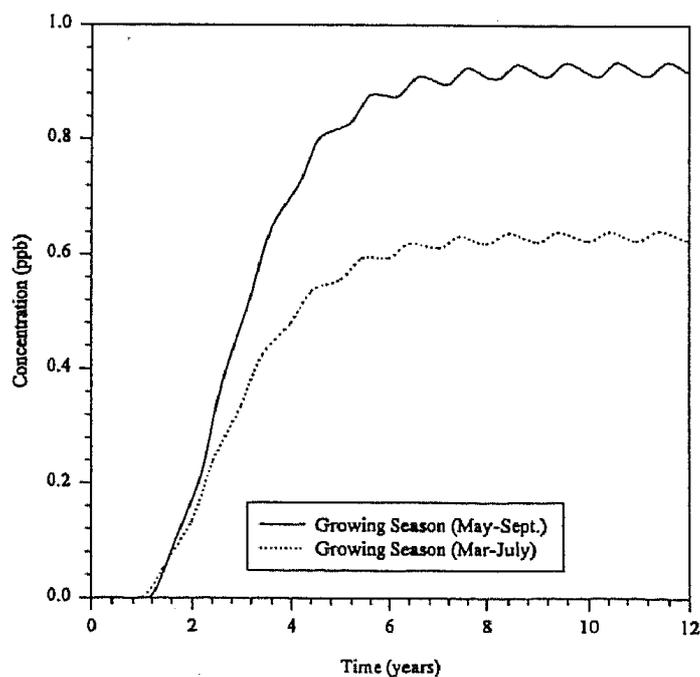


Figure 8. Effect of agricultural practice on predicted exposure levels (ppb) of bromacil in the hypothetical drinking water well.

groundwater. Because bromacil is mobile and relatively persistent, leaching below the root zone is an important mechanism for the emission of the chemical to the water table. Although not shown in table 4, the second inactive season (August 1–February 28) includes two relatively drier months, August and September. While the inactive season of the first scenario (October 1–April 30) favors greater leaching below the root zone, because of relatively greater average precipitation (0.4 m), the inactive season of the second scenario is characterized by less average precipitation (0.32 m). Consequently, the latter favors increased long-term losses of the pesticide by degradation due to increased residence time in the sandy soil. The reduced leaching rate also justifies the less rapid buildup in bromacil concentrations (figure 8).

There are two shortcomings worth emphasizing while analyzing figures 4–8. First, linear-reservoir models ignore the development of the dispersion process; thus, they tend to underestimate peak concentrations and predict earlier breakthrough. Second, linear equilibrium isotherms do not limit the amount of a solute that can be sorbed onto solid; hence, they predict less soluble concentrations by overestimating the amount of the solute sorbed onto the solid. Consequently, non-linear sorption isotherms may predict relatively greater groundwater concentrations than those displayed in figures 4–8.

6 Conclusion

Potential contamination of groundwater is an important environmental aspect of the use of pesticides for agricultural purposes. Physically-based transport and fate simulation models are useful tools for regulatory agencies and policy makers before approving the use of pesticides, because they aid the assessment of long-term vulnerability of drinking-water wells to hazardous exposure levels. An analytical model was developed which described leaching of pesticides in the soil-root zone and intermediate vadose zone, and their migration in groundwater. Existence of pesticides in the vapor phase is allowed for through a liquid-vapor partition, using Henry's Law, and volatilization is assumed to occur by diffusion of pesticides in the vapor phase through an air-boundary layer. Passive (first-order) uptake is modeled by assuming a linear relationship between the rate of uptake and soluble concentrations. First-order degradation and equilibrium sorption isotherms are also accounted for in the soil and the aquifer. Although the model is based on some rigid assumptions (uniform properties in each of the soil zones, steady state flow, and complete mixing in each zone), it nevertheless predicts concentrations in groundwater analytically, requiring a small set of data, and accounting in a rather simple manner for the complex interactions among the different physical, (bio)chemical, and meteorological

processes. The model was applied to a group of five pesticides (atrazine, bromacil, chlordane, heptachlor, and lindane), primarily, to investigate the effect of crop uptake, volatilization from the soil surface, type of soil environment, and agricultural practices on long-term predictions of the pesticide exposure levels in groundwater. Pesticides with short half-life such as atrazine, bromacil, and lindane showed very low predicted levels in groundwater, however, highly variable in time because of the seasonal effect of the leaching mechanism and agricultural practices. Although lindane has a relatively greater degradation rate, the slowly degradable and highly mobile heptachlor showed relatively lower predicted concentrations in groundwater because of its high volatilization from the root zone. Further, predicted concentrations showed that crop uptake can have a profound effect on reducing long-term vulnerability of groundwater to slowly degrading pesticides like bromacil. While a clayey soil environment favored substantial losses by degradation and volatilization, hence, much smaller long-term predicted concentrations in groundwater, the mechanism of crop-root uptake showed greater efficiency in a sandy soil in reducing long-term bromacil and atrazine exposure levels, than in a clayey soil. Under climatic conditions similar to the ones assumed here, changing agricultural practices, whereby increasing portions of consumption by crops can be met by infiltrating rain, resulted in substantially lower exposure levels of bromacil in groundwater.

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