
MODELING FATE AND TRANSPORT OF ATRAZINE IN THE SATURATED-UNSATURATED ZONE OF SOIL

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ABSTRACT Atrazine is a widely-used herbicide for selective control of broadleaf and grassy weeds, and it has been detected in ground water. Experimental work in this area shows that the degradation of atrazine is dependent on the soil water content. Of specific interest to this study is the influence of fluctuating water tables on atrazine degradation. A 1-D finite-difference model has been developed to study saturated-unsaturated water movement and transport of atrazine with kinetic-nonlinear adsorption and water content-dependent degradation. The water movement and chemical transport have been decoupled so that the water fluxes are treated independent of the chemical concentrations. Model results of the fate and transport of atrazine for various physical scenarios are included in the form of graphs.

KEYWORDS: atrazine, solute transport, saturated-unsaturated model

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine) is a herbicide used for selective control of broadleaf and grassy weeds and has been detected in ground water. An evaluation of the potential for atrazine and other pesticides to contaminate ground water requires an understanding of the transport mechanisms that occur in the field and the capability to accurately represent these mechanisms in simulation models [1].

Study on fate and transport of atrazine show that the degradation of atrazine is dependent on the soil water content [2-5]. Of particular interest in this study is the effect of changing moisture conditions on the degradation of atrazine in soil. A physical scenario for such a process is the effect of a fluctuating water table on the degradation of atrazine in the capillary fringe zone. Atrazine is used in this study because it is one of the more persistent and widely used herbicides, and it is decomposed both chemically as well as

microbiologically. Therefore, the effect of an alternate water content, if any, should become evident.

Alternating the moisture levels in definite cycles results in quite different degradation rates for the dry periods [5]. Possibly these discrepancies are caused by the changes in the organic matter due to drying and rewetting of the soil. Drying will spread the organic particles, leading to an increased internal surface with additional catalytic sites for pesticide degradation. By rewetting the soil, more of the pesticide comes in contact with these sites, leading to faster degradation during the next dry period.

MODEL FORMULATION

Almost any modeling activity related to ground water starts with a water flow model since for any significant change to take place in the flow field, flow is an essential ingredient. Decoupling the water and chemical transport is a model simplification. This means that the influence of the chemical on water flow is insignificant, and

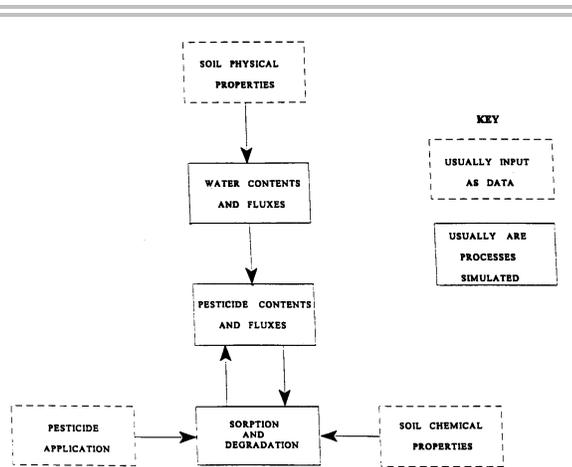


FIGURE 1. SCHEMATIC REPRESENTATION OF THE PROCESSES THAT INFLUENCE PESTICIDE FATE IN SOILS.

properties such as density gradients that can cause fluid movement can be ignored. Thus the water fluxes are first calculated independent of the chemical concentrations and then these water fluxes are used in calculating the chemical fluxes. The model was written in FORTRAN for interactive use on a microcomputer.

Processes identified as being the primary determinants of pesticide behavior in soils include (i) degradation of a pesticide by soil microorganisms that use it as a substrate for their growth and maintenance; (ii) chemical degradation, a process that results from the participation of the pesticide in common chemical reactions (e.g., hydrolysis) that can occur in the aqueous phase; (iii) pesticide sorption which leads to reduced mobility of the pesticide; (iv) the diluting effects of water flow processes that act to disperse and distribute the pesticide during its passage through the unsaturated zone toward ground water. These processes are depicted schematically in Figure 1.

GOVERNING DIFFERENTIAL EQUATIONS

Water flow equations

Saturated-unsaturated ground water flow (1-D):

$$\left[\frac{\theta(\psi)}{\eta} S_s + C(\psi) \right] \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left[k_z(\psi) \left(\frac{\partial \psi}{\partial z} - 1 \right) \right], \quad (1)$$

where ψ = matric potential, η = porosity, S_s = specific storage of the soil, $\theta(\psi)$ = soil water content, $C(\psi)$ = specific moisture capacity of soil = $d\theta/d\psi$, $q(t)$ = ground water flux, k_z = hydraulic conductivity, and z = vertical co-ordinate.

The subsurface flow of water takes place in the pores or voids of the soil medium. This component is complicated by the presence of two distinct regions—the saturated and the unsaturated zones [6]. The water table is a theoretical surface at which the pressure in the soil water equals the atmospheric pressure. In the unsaturated zone, flow is driven by the gravitational potential and the negative hydrostatic potential due to capillary suction. In the saturated zone, the flow is governed by the piezometric head or the total energy head, which is composed of the elevation head and the positive pressure potentials.

The saturated-unsaturated equation shown above is obtained by combining the continuity equation of mass conservation and Darcy's law. This equation is highly non-linear as it involves the hydraulic properties of the soil which are a function of ψ (suction head of the soil).

SOIL HYDRAULIC PROPERTIES

Soil hydraulic functions refer to the soil water retention curve, $\theta(\psi)$, and the

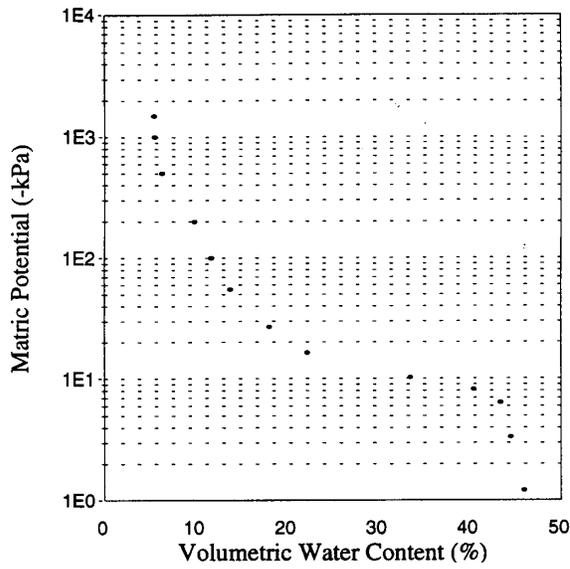


FIGURE 2. SOIL WATER RETENTION CURVE.

hydraulic conductivity function, $k(\psi)$. These functional forms are needed to solve for water movement. Several functions have been proposed to empirically describe the soil hydraulic properties. One of the more popular models are the equations of Brooks & Corey [7]:

$$k(\psi) = k_s \left(\frac{\psi_b}{\psi} \right)^{2+3\lambda}, \quad (2)$$

$$\theta(\psi) = \theta_0 + (\theta_s - \theta_0) \left(\frac{\psi_b}{\psi} \right)^\lambda, \quad (3)$$

where ψ = matric potential, ψ_b = air entry suction pressure head, θ_s = saturated water content, θ_0 = residual water content, λ = empirical parameter, and k_s = saturated hydraulic conductivity.

The relation between soil water content and the soil water suction is a fundamental part of the characterization of the hydraulic properties of a soil [8]. Determining the water retention function involves establishing a series of equilibria between water in the soil sample and a body of water

at a known potential. At each equilibrium, the volumetric water content, θ , of the soil is determined and paired with a value of the matric pressure head, ψ , determined from the pressure in the body of water. The data pair (θ, ψ) is one such point on a retention curve.

In the present study, pressure plate apparatus has been used to determine the soil water retention curve. Thirteen data pairs were determined and plotted to get a soil water retention curve as shown in Figure 2.

SOLUTE TRANSPORT EQUATIONS

Advection-dispersion equation:

$$\frac{\partial}{\partial t} [\theta C + \rho S] = \frac{\partial}{\partial z} \left[\theta D \frac{\partial C}{\partial z} - qC \right] - \mu_1(\theta) C - \mu_2 \rho S, \quad (4)$$

$$\frac{\partial S}{\partial t} = \alpha [f(C) - S], \quad (5)$$

where ρ = bulk density, D = dispersion coefficient, α = transfer rate coefficient, C = concentration of atrazine in liquid phase, S = concentration of atrazine in solid phase, $\mu_1(\theta)$ = decay rate in liquid phase, μ_2 = decay rate in solid phase, and $f(C)$ = adsorption isotherm for atrazine.

The above equation describes the change in mass of a contaminant in a unit volume of soil per unit time. The first term on the right-hand side of Equation 4 describes the dispersive flux into the elemental volume. The second term describes the mass transfer of atrazine out of the representative volume by fluid flow (often called advective transport). The third and fourth terms describe the mass loss rate of transfer of molecules from the aqueous phase to the solid phase and the mass rate of gain caused

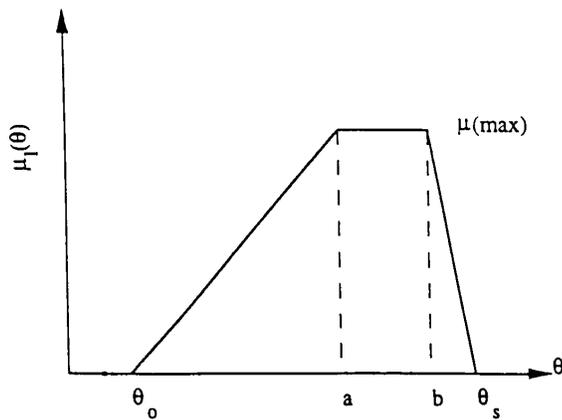


FIGURE 3. DEGRADATION RATE OF ATRAZINE IN LIQUID PHASE (μ_1) VS. SOIL WATER CONTENT (θ).

by transfer of molecules from the solid phase to liquid phase, respectively [9].

ATRAZINE ADSORPTION ISOTHERM

The sorption of the pesticide on the soil retards its movement through the root zone, with the extent of retardation dependent upon the physical and chemical properties of the soil as well as the molecular characteristics of the pesticide. The Freundlich equation has satisfactorily described experimental results of pesticide sorption in many cases. Hence in the present model, the Freundlich isotherm has been used to describe atrazine adsorption. The Freundlich equation is as follows:

$$f(C) = k_f (C)^{\frac{1}{n}}, \quad (6)$$

where K_f = Freundlich coefficient and $1/n$ = Freundlich exponent.

WATER CONTENT-DEPENDENT DEGRADATION OF ATRAZINE

Figure 3 shows the conceptualized water content-dependent degradation rate of

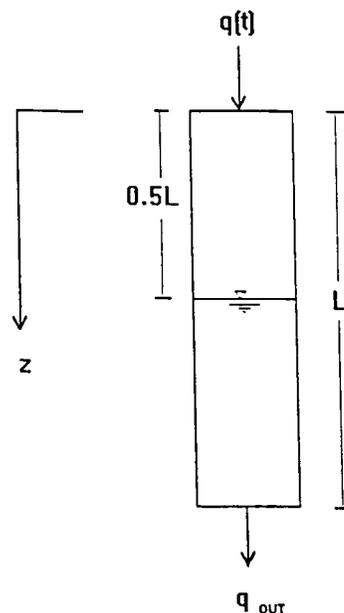


FIGURE 4. HYPOTHETICAL SOIL COLUMN.

atrazine in the liquid phase. Moisture is necessary for microbial activity and other soil processes including diffusion of gaseous oxygen into water. The degradation rate for dry soils is low as it is expected that the microbial activity is extremely low in dry environments. Under aerobic conditions, as the water content increases the degradation rate increases. However, at higher water contents (i.e., under saturated conditions), air diffusion within soil pores will be restricted and with higher biological activity, dissolved oxygen deficit occurs with insufficient diffusion of air into soil pores (anaerobic conditions), leading to very little or no degradation of atrazine.

PHYSICAL PROBLEM

Figure 4 shows a hypothetical soil column.

BOUNDARY CONDITIONS

Ground water flow

At $z = 0$,

$$q(t) = -k_z(\psi) \left(\frac{\partial \psi}{\partial z} - 1 \right). \quad (7)$$

At $z = L$,

$$q = 0.1 \text{ cm/hr}. \quad (8)$$

Atrazine transport

At $z = 0$,

$$vC_0 = vC - D \frac{\partial C}{\partial z}, \quad (9)$$

where $v = q/\theta$.

At $z = L$,

$$\frac{\partial C}{\partial z} = 0 \quad (10)$$

INITIAL CONDITIONS

Ground water flow

Static initial conditions:

$$\phi(z, 0) = -\frac{L}{2}, \quad (11)$$

$$\psi(z, t) = \phi + z, \quad (12)$$

where ϕ = total head.

Atrazine transport

$$S(z, 0) = 0.0, \quad (13)$$

$$C(z, 0) = 0.0. \quad (14)$$

METHOD OF SOLUTION

A finite difference technique is used to study the saturated-unsaturated water movement and transport of atrazine with kinetic-nonlinear adsorption and water content-dependent degradation.

Ground water flow

Newton's method is used to solve the water flow equations.

Atrazine transport

The solute transport equations are solved using the Picard's scheme.

SIMULATION PARAMETERS

The input data requirements are listed in Table 1.

Input flux

Three cases representing different fluctuations of the water table are shown in Figure 5.

Case 1: The flux increases from zero to a value of 1.0 cm/hr in 1.5 hr and remains constant at that value.

Case 2: This is a case of a cyclic fluctuation. The flux increases, decreases, and remains constant at zero for some time and again follows the same pattern for three cycles. The

TABLE 1. SIMULATION PARAMETERS.

$L = 50 \text{ cm}$	$\theta_s = 0.5$	$k_s = 2.0 \text{ cm/hr}$	$f(C) = 0.82 (C^{0.92})$
$dt = 0.0005 \text{ hrs}$	$\theta_0 = 0.04$	$S_s = 0.01/\text{cm}$	$D = 0.05 \text{ cm}^2/\text{hr}$
$\rho = 1.3 \text{ g/cm}^3$	$\eta = 0.5$	$\mu_{1(\text{max})} = 0.01/\text{hr}$	$C_0 = 1.0 \text{ g/cm}^3$
$\psi_b = -5.0 \text{ cm}$	$\lambda = 0.5$	$\mu_2 = 0.0$	$\alpha = 0.3/\text{hr}$

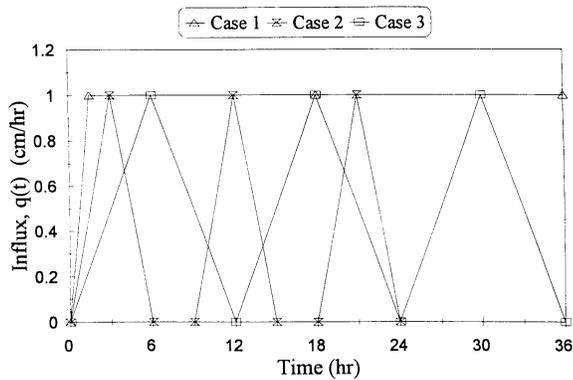


FIGURE 5. INPUT FLUX $q(t)$ VS. TIME (t)—THREE CASES OF SIMULATION.

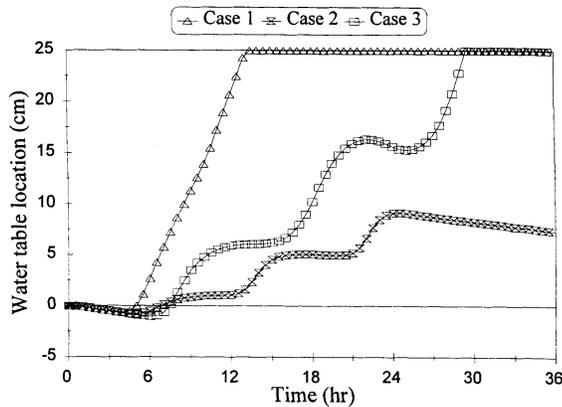


FIGURE 6. WATER TABLE LOCATION VS. TIME.

interval of fluctuation is three hours.

Case 3: This is also a case of a cyclic fluctuation. The flux increases and decreases continuously for three cycles. The interval of fluctuation is six hours.

PRELIMINARY RESULTS

The preliminary results are shown in Figures 6 through 11.

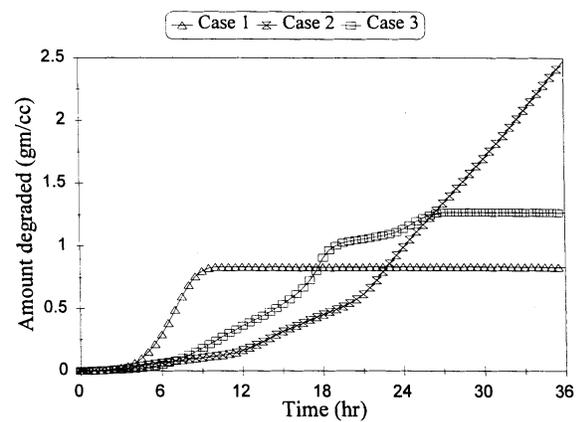


FIGURE 7. AMOUNT OF ATRAZINE DEGRADED VS. TIME.

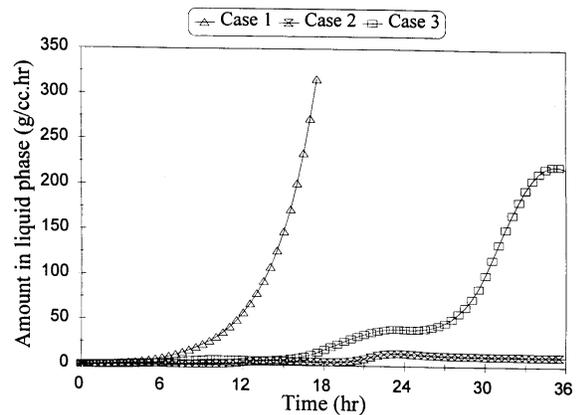


FIGURE 8. AMOUNT OF ATRAZINE IN LIQUID PHASE VS. TIME.

CONCLUSIONS AND FUTURE RESEARCH

A numerical model was developed to simulate water movement and fate and transport of atrazine under fluctuating water table conditions. Examination of the model results lead to the following conclusions:

1. The model suggested that atrazine degradation increases for the case of a fluctuating water table. This will be confirmed from the experimental results.

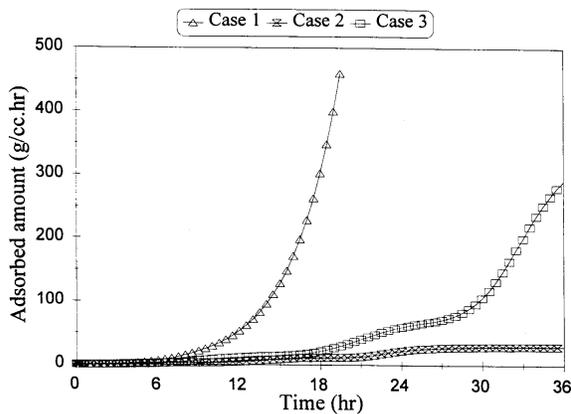


FIGURE 9. AMOUNT OF ATRAZINE IN SOLID PHASE VS. TIME.

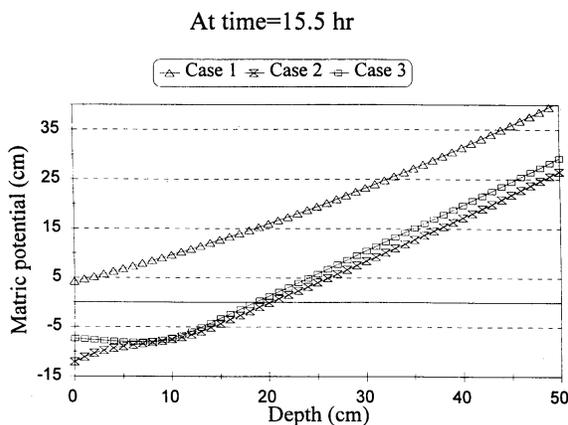


FIGURE 10. PRESSURE HEAD VS. DEPTH AT TIME = 15.5 hr.

2. The model is highly nonlinear and fairly computer-intensive, requiring very small time steps (≈ 0.0005 hrs) initially for convergence.

The representative parameters used in this model will be replaced by the values obtained from the experimental study to perform model validation. Further work needs to be done on improving model performance. More accurate numerical schemes to reduce numerical dispersion are being investigated. More research on this subject is needed, including other herbicides and soils, to achieve a better understanding

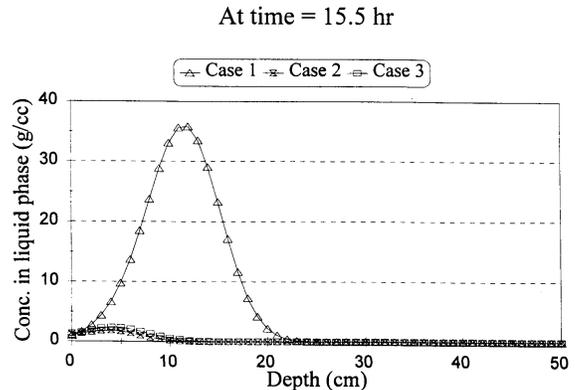


FIGURE 11. CONCENTRATION OF ATRAZINE IN LIQUID PHASE VS. DEPTH AT TIME = 15.5 hr.

of herbicide degradation under varying conditions in the field.

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