

# **A STEADY-STATE UNSATURATED-ZONE MODEL TO SIMULATE PESTICIDE TRANSPORT**

**By A.T. Rutledge and J.O. Helgesen**

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## CONVERSION FACTORS

For those readers who may prefer metric units (International System), the inch-pound units of those report may be converted using the following factors:

<i>Multiply inch-pound unit</i>	<i>By</i>	<i>To obtain metric unit</i>
inch	2.54	centimeter
foot	0.3048	meter
acre	4,047	square meter
pound	453.6	gram
cubic foot per pound	62.43	cubic centimeter per gram
pound per cubic foot	0.01602	gram per cubic centimeter
pound per acre	0.112	gram per square meter

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# A STEADY-STATE UNSATURATED-ZONE MODEL TO SIMULATE PESTICIDE TRANSPORT

By A.T. Rutledge and J.O. Helgesen

## ABSTRACT

A simple model of pesticide transport in the unsaturated zone is described; its use in an example problem is demonstrated; and sensitivity to selected variables is presented. The model calculates time of travel and fraction of pesticide remaining in the unsaturated zone as functions of depth. The model is best used for screening purposes, and it is not intended for detailed, site-specific analysis. The model allows for multiple lithologic layers in the unsaturated zone, water-content variation with depth, pesticide retardation caused by partitioning, pesticide-decay rates that vary between layers, and root uptake of pesticides. The variables to which the model is most sensitive are deep-percolation rate, organic-carbon content in the lower part of the unsaturated zone, pesticide half-life, and depth to the water table.

## INTRODUCTION

Widespread concern about contamination of water supplies has drawn increased attention to the effects of agricultural chemicals on ground water. Routine use of pesticides in agricultural areas has introduced nonpoint-source contamination of water supplies. Identification and measurement of nonpoint-source contamination have been difficult because the processes affecting pesticides and ground water are complex.

Nonpoint-source ground-water contamination from pesticides has been documented in several agricultural areas, such as parts of Nebraska and Iowa (Chen and Druliner, 1987; Hallberg and others, 1987). In other areas, such as south-central Kansas (Stullken and others, 1987), pesticides have been detected infrequently in ground water. Concentrations of pesticides, where present, are nearly always very small, commonly less than 1  $\mu\text{g/L}$  (microgram per liter).

The occurrence of pesticides in the High Plains aquifer in south-central Kansas was evaluated (Stullken and others, 1987; Helgesen and Rutledge, 1989) as part of the U.S.

Geological Survey's Toxic Waste--Ground-Water Contamination Program (Helsel and Ragone, 1984).

Common use of the herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-s-triazine) on row crops grown in south-central Kansas generally is not reflected in the quality of the underlying ground water. This fact has directed attention toward the intervening unsaturated zone as the principal medium within which the movement and fate of the pesticide is determined.

Subsurface distribution of pesticides within the unsaturated zone is the result of many factors and variables (Cheng and Koskinen, 1986; Severn, 1987), which as yet are poorly understood. Variables that may be important include: rate of downward water flux, soil properties, and sorption and degradation properties of pesticides. A combination of retardation (caused by pesticide partitioning between the aqueous and solid phases) and degradation (caused by biochemical reactions), for example, may account for the absence of a pesticide in the saturated zone beneath an area of known application.

The time of travel of a pesticide in the unsaturated zone is one indicator of the potential for ground-water contamination. The time of travel must be short enough in relation to the period of antecedent pesticide application for contamination to be possible. Another indicator of relative ground-water contamination potential is the fraction of pesticide remaining in the unsaturated zone just above the water table. This fraction may be extremely small because of the combined effects of retardation, decay, and root uptake.

As a preliminary effort in estimating the effect of selected variables on pesticide transport, a simple mathematical model was developed and tested. The model calculates time of travel of surface-applied pesticides and the fraction of pesticide remaining as functions of depth through the unsaturated zone. Because the model was developed as part of an effort to

evaluate regional nonpoint-source contamination, it is intended to be a screening tool rather than a rigorous site-specific simulator. Results from the model can help rank, by order of importance, variables that affect pesticide occurrence (among the variables evaluated by the model), and thereby aid in interpreting measured ground-water quality. Also, model results could help direct future efforts to develop an improved understanding of the processes of pesticide transport.

This report: (1) Describes a mathematical model of unsaturated-zone pesticide transport; (2) demonstrates use of the model with example data; and (3) presents results of analyses of model sensitivity to selected variables. To test sensitivity, large ranges in values of model variables were used so that results might reflect conditions throughout the agricultural region of the Midwestern United States. Although some model results are presented for several different pesticides, atrazine was the primary compound for the sensitivity analyses.

## DESCRIPTION OF MODEL

### Assumptions

The mathematical model described here is based on the following assumptions:

- (1) Water content in the unsaturated zone may be described as a static function of elevation above the water table.
- (2) Water flux is steady, is downward, and is diminished linearly with depth in the root zone.
- (3) All water in the unsaturated zone transports pesticides.
- (4) Water initially present in the profile is completely displaced downward by water entering from above.
- (5) Pesticides of interest are in the aqueous phase or are adsorbed; they are not in a nonaqueous liquid phase or gaseous phase.
- (6) Adsorption is described by a linear, reversible equilibrium relation.

- (7) Pesticide decay is an irreversible first-order reaction.
- (8) Pesticides occur at concentrations small enough that the capacities for adsorption and decay of the pesticides by materials in the unsaturated zone are not exhausted.
- (9) Root uptake of pesticide is proportional to the root uptake of water (the loss of water in the root zone).
- (10) Pesticides are applied at land surface at a constant rate; pesticide flux is steady state everywhere; and dispersion of pesticides is neglected.

This simple mathematical model is useful provided the user is aware of these assumptions. The assumptions may limit the applicability of the model results; however, these limitations become less significant if model results are used in a comparative sense.

### Time of Travel of Pesticide in the Unsaturated Zone

A differential equation relating time to distance of travel is derived from:

$$v = \frac{dz}{dt} \quad , \quad (1)$$

where  $v$  = vertical velocity ( $LT^{-1}$ ),

$z$  = depth below land surface (L), and

$t$  = time (T).

This equation may be integrated to obtain:

$$t_i = \int_0^{z_i} \frac{1}{v} dz \quad , \quad (2)$$

where  $t_i$  = time of travel (T) for transport from land surface to a depth of interest, and

$z_i$  = depth of interest below land surface (L).

The vertical velocity can also be expressed as:

$$v = \frac{q}{(\theta)(R)}, \quad (3)$$

where  $q$  = the volumetric water flux per unit surface area ( $LT^{-1}$ ),

$\theta$  = the volumetric water content (dimensionless), and

$R$  = the retardation factor of the pesticide's transport (dimensionless), which is the ratio of the average velocity of water to the average velocity of pesticide.

Water flux ( $q$ ) at the land surface ( $z=0$ ) is set equal to the rate at which water enters the ground and, at the bottom of the root zone, is set equal to the rate of deep percolation. For all depths within the root zone, water flux is interpolated linearly between these two values. Water flux below the root zone is equal to the rate of deep percolation.

The model determines the volumetric water content at a given point as a function of elevation of that point above the water table ( $h$ ). The model treats the pressure-head profile above the water table as being in static equilibrium. An example of a water-characteristic curve for a layer (interval of consistent lithology) is given in figure 1, which illustrates how the relation is a

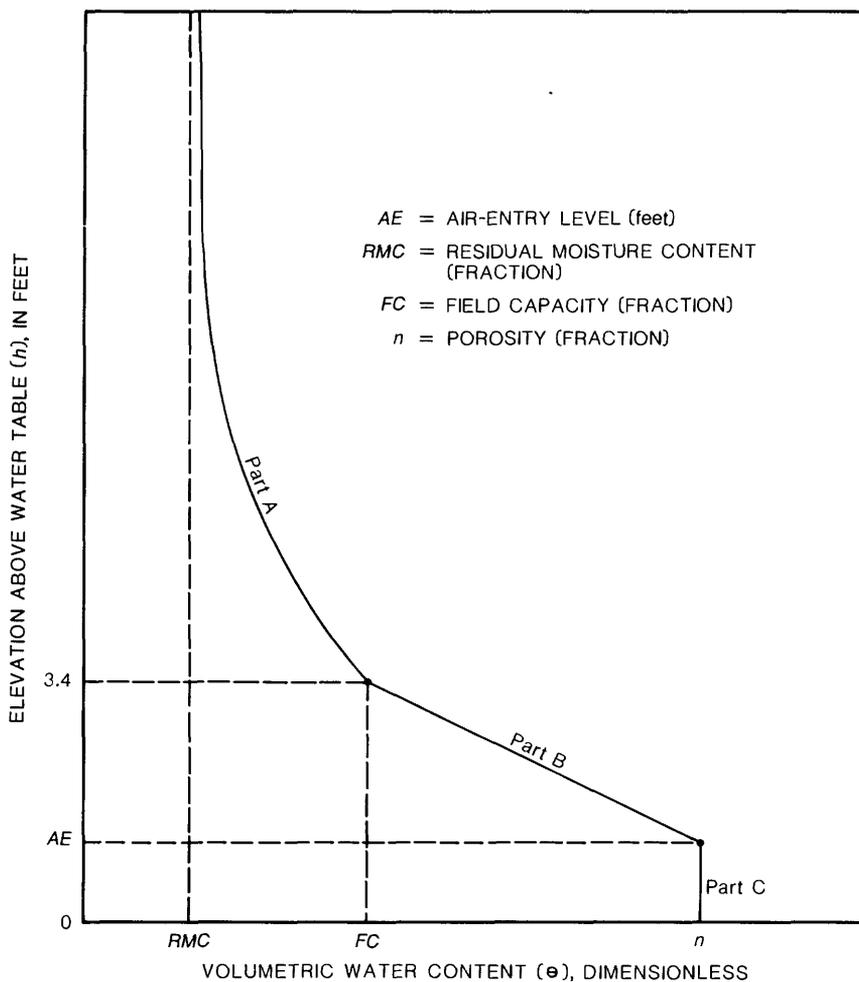


Figure 1. Model calculation of water content in the unsaturated zone as a function of elevation above water table given air-entry level, residual moisture content, field capacity, and porosity.

function of the layer's air-entry level, residual moisture content, field capacity, and porosity. The water-characteristic curve is made up of three parts:

Part A of the curve is asymptotic to a water content equal to the residual moisture content and passes through the point where  $\theta$  = field capacity at  $h = 3.4$  feet (fig. 1). This is the elevation above the water table at which the matric potential is specified to be -0.1 bar, under equilibrium conditions. Part A of the curve also is asymptotic to  $h = 0$ .

Part B of the water-characteristic curve is a straight line connecting  $\theta$  = field capacity at  $h = 3.4$  feet, and  $\theta$  = porosity at  $h$  = air-entry level (fig. 1). The latter point is the highest

elevation above the water table at which water content is equal to porosity and corresponds to the height of the capillary fringe.

Part C of the curve is a straight vertical line connecting  $\theta$  = porosity at  $h$  = air-entry level, with  $\theta$  = porosity at  $h = 0$ . Water content is equal to porosity in part C.

Because water-characteristic curves may differ from one layer to another, there can be discontinuities in the relation between elevation and water content when the simulated system consists of multiple layers. The relation between elevation and water content for an example configuration consisting of four layers is shown in figure 2.

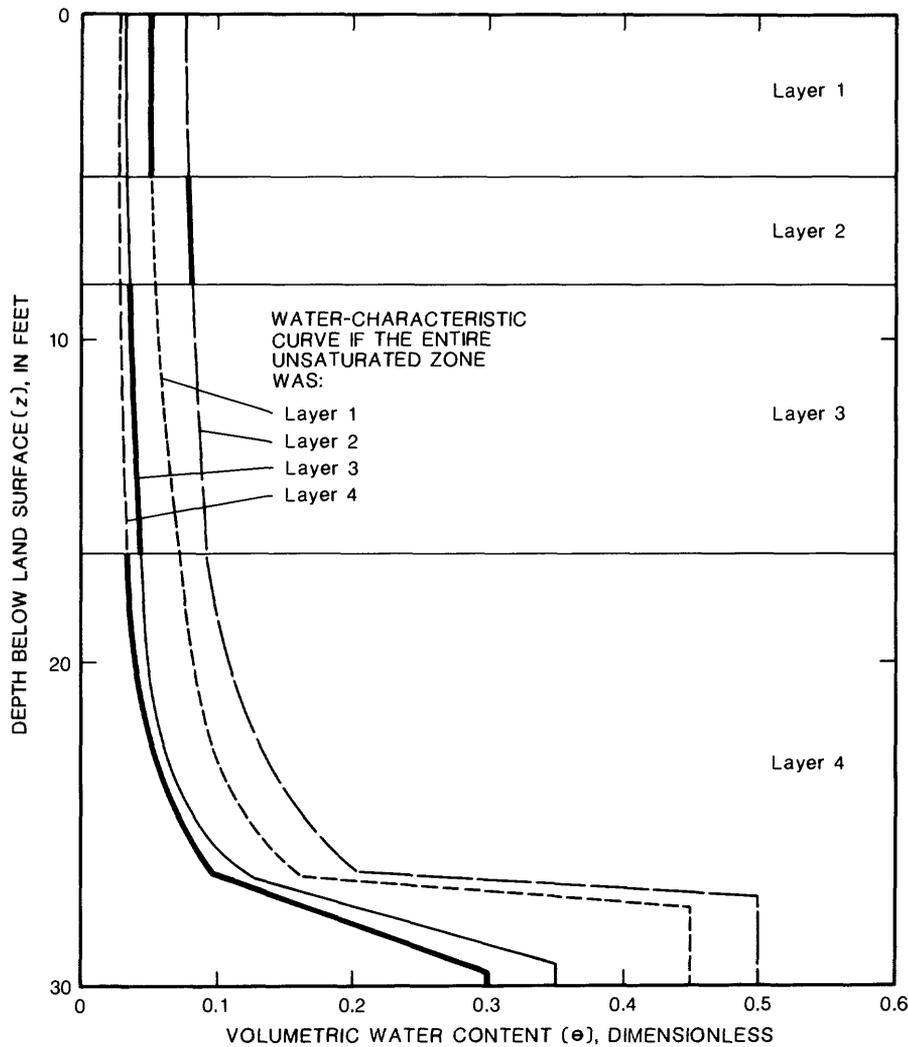


Figure 2. Steady-state water-characteristic curves for a simulated unsaturated zone consisting of four layers.

The retardation factor ( $R$ ) is

$$R = 1 + \frac{(\rho_b)(K_d)}{\theta}, \quad (4)$$

where  $\rho_b$  = bulk density ( $\text{ML}^{-3}$ ), and

$K_d$  = distribution coefficient ( $\text{L}^3\text{M}^{-1}$ ), assuming that the adsorption process may be expressed as a linear isotherm.

Bulk density and distribution coefficient are constant within any given layer but may vary from one layer to another. Bulk density,  $\rho_b$ , is calculated from:

$$\rho_b = \rho_s (1 - n), \quad (5)$$

where  $\rho_s$  = density of the solid material in the unsaturated zone ( $\text{ML}^{-3}$ ), and  
 $n$  = porosity.

It is assumed that  $\rho_s = 165$  pounds per cubic foot.  $K_d$  is calculated for each layer from:

$$K_d = (K_{oc})(P_{oc}) / 100, \quad (6)$$

where  $K_{oc}$  = organic-carbon partition coefficient ( $\text{L}^3\text{M}^{-1}$ ) of the pesticide (a constant for a given simulation), and

$P_{oc}$  = percentage of organic carbon in the layer.

Combining equations 2, 3, and 4:

$$t_i = \int_0^{z_i} \frac{1}{q [\theta + (\rho_b)(K_d)]} dz. \quad (7)$$

The model solves equation 7 to determine the time of a pesticide's transport to a given depth. The terms  $q$ ,  $\theta$ ,  $\rho_b$ , and  $K_d$  are variable with depth, so the solution is by numerical integration.

## Fraction of Pesticide Remaining

The fraction of pesticide remaining at the depth of interest is calculated using equations

representing two attrition processes--decay and root uptake.

The fraction of the original pesticide that remains after the decay that occurs during its transport through a layer of the unsaturated zone (or to a particular point within the layer) can be calculated by solving the differential equation for irreversible first-order reactions (Tchobanoglous and Schroeder, 1985, p. 242):

$$\frac{dC}{dt} = -k(C), \quad (8)$$

where

$C$  = concentration of pesticide ( $\text{ML}^{-3}$ ),

$t$  = time of travel in the layer of interest (T), and

$k$  = a constant.

After integrating, rearranging, and substitution, this equation yields

$$RM = e^{-k(t)}, \quad (9)$$

where  $RM$  = fraction of pesticide remaining after its transport through the layer. Because  $RM = 0.5$  at  $t = \text{half-life}$ , the equation can be rewritten:

$$RM = e^{-0.693(t)/t_{\frac{1}{2}}}, \quad (10)$$

where

$t_{\frac{1}{2}}$  = half-life of pesticide in the layer (T).

Equation 10 is solved for each layer, allowing for the time of travel in each. The amount of the original pesticide applied to the land surface that remains after transport through more than one layer is the product of the values of  $RM$  for each layer.

Root uptake of pesticide is assumed to be proportional to the root uptake of water. To obtain the fraction remaining after decay and root uptake, the amount of pesticide remaining after decay is multiplied by a ratio of the amount of water flux at the depth of interest to the rate at which water enters the ground at the land surface.

## MODEL APPLICATION

### Example Simulation

An example of the use of the model to simulate the transport of five chemicals in a four-layer unsaturated zone is shown in figure 3. The four layers correspond to lithologies that may occur in the High Plains aquifer in south-central Kansas. Physical characteristics of the system are given in table 1. Water content, for the configuration shown in figure 3, is shown in figure 2. The properties of the five chemicals depicted in figure 3 are given in table 2.

The results shown in figure 3 demonstrate a large range in transport velocities and decay

rates among the various chemicals. Chloride, which is a conservative tracer ( $K_{oc} = 0$ ), has the shortest time of travel (2.4 years) in the unsaturated zone (30 feet), whereas trifluralin penetrates less than 2 feet in 15 years. Of the three pesticides reaching the water table, atrazine has the largest fraction remaining. Given an atrazine application rate of 2 pounds per acre per year, and assuming that the atrazine remaining after transport through the unsaturated zone is uniformly distributed in water reaching the water table, the fraction remaining equates to a concentration of 0.25  $\mu\text{g/L}$  in recharge water. Although the time of travel of 2,4-D amine is considerably less than that of atrazine, the rate of decay allows much less 2,4-D amine to reach the water table.

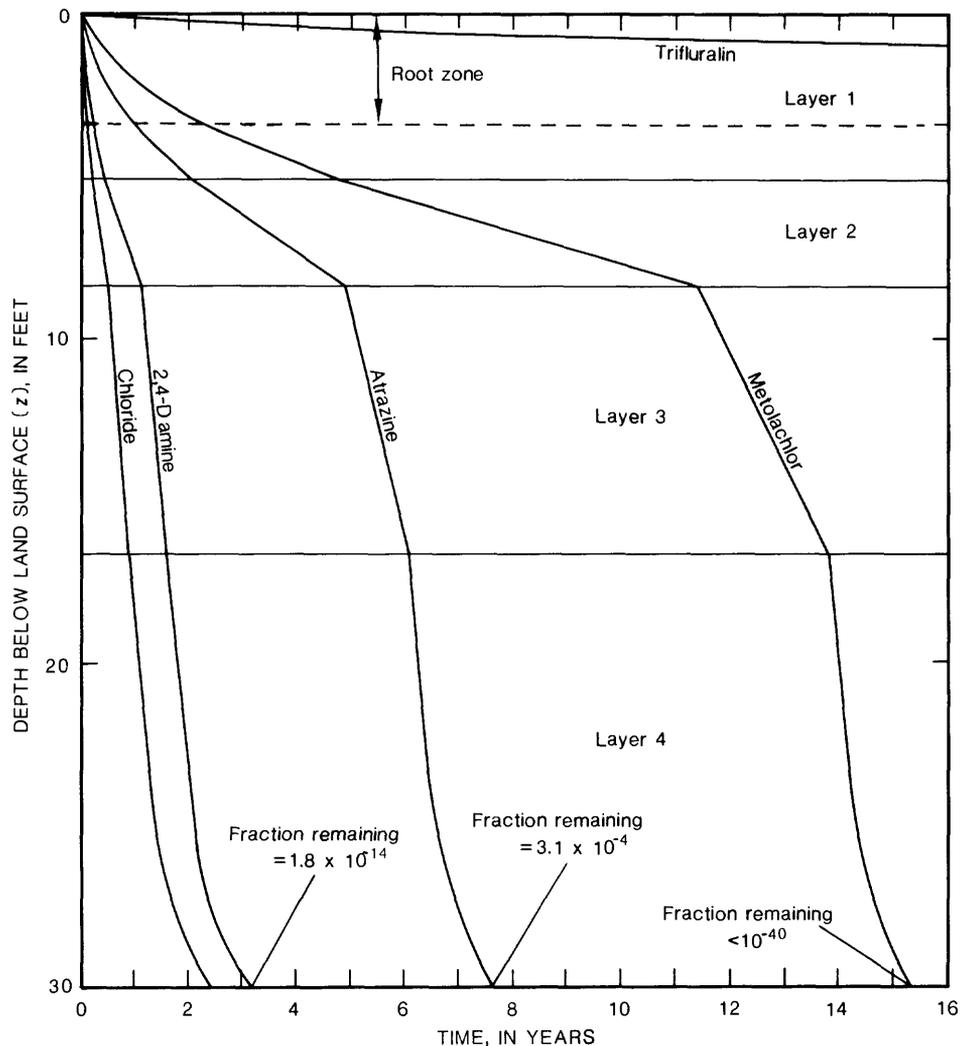


Figure 3. Transport of five chemicals in a simulated four-layer unsaturated zone.

The potential for a given pesticide to contaminate ground water, as defined by this model, increases as the pesticide's organic-carbon partition coefficient decreases and its half-life increases. The values of these variables depend on local conditions, such as the amount of pesticide applied, the depth to the water table, and the organic-carbon content of the unsaturated zone.

Several changes in contaminant velocity are shown in figure 3. Velocity varies considerably from land surface to the bottom of the root zone because of variations in water flux. Abrupt changes in velocity occur between layers because of changes in water content (fig. 2). A gradual decline in velocity approaching the water table occurs because of an increase in water content in the capillary fringe.

### Sensitivity Analyses

The sensitivity of the model of atrazine to selected variables in a simple two-layer system

was tested in terms of unsaturated-zone transport of atrazine. The upper layer, which is 3 feet thick, corresponds to the soil and root zone; the lower layer, which is 97 feet thick, represents the remainder of the unsaturated zone to the water table.

Reasonable, though arbitrary, values for each required variable (geohydrologic, soil, and pesticide properties) were selected for the sensitivity analyses. These values are identified as intermediate values in table 3. The two layers were assigned different values of organic-carbon content and atrazine half-life. The upper layer (soil) is characterized by considerably larger organic-carbon content than the lower layer (parent material). Half-life is less in the upper layer than in the lower layer. Other variables are considered vertically uniform for purposes of this analysis. Information was also assembled to estimate reasonable expected ranges in values (table 3) applicable to the agricultural region of the Midwestern United States. The assigned intermediate values and the expected ranges of

**Table 1. Physical characteristics of a four-layer unsaturated zone (fig. 3)**

Rate at which water enters the ground		40.0 inches per year					
Rate of deep percolation below roots		10.0 inches per year					
Thickness of root zone		3.0 feet					
Depth to water table		30.0 feet					
Density of solid material in the unsaturated zone		165 pounds per cubic foot					
-----							
Layer number	Type of material	Depth to bottom (feet)	Air-entry level (feet)	Residual moisture content (dimensionless)	Field capacity (dimensionless)	Porosity (dimensionless)	Organic-carbon content (percent)
1	Sandy loam	5.00	2.50	0.04	0.16	0.45	0.20
2	Silty loam	8.00	3.00	.06	.20	.50	.30
3	Medium sand	16.00	.70	.02	.12	.35	.03
4	Coarse sand	30.00	.20	.02	.10	.30	0

**Table 2.** *Properties of five chemicals in a four-layer unsaturated zone (fig. 3)*

[N/A, not applicable]

Property	Chloride	2,4-D amine	Atrazine	Metol- achlor	Triflur- alin
Organic-carbon partition coefficient, in cubic feet per pound (all layers)	0	0.35	2.56	6.41	256
Half-life, in days (layer 1)	N/A	16	182	18	120
Half-life, in days (layers 2-4)	N/A	30	365	42	240

values (table 3) resulted from discussions with several workers familiar with hydrologic or soils properties in the region, and from numerous references, including: U.S. Soil Conservation Service (1981), Cohen and others (1984), Gutentag and others (1984), Dugan and Peckenpaugh (1985), Jury and others (1986), Luckey and others (1986), and Nilson and others (1986).

The sensitivity of the model to a given variable was tested by assigning intermediate values to all other variables (table 3), then comparing the model results when the two extreme values for the selected variable were used. Thus, the analysis neglects any interdependence between variables. For example, when the model's sensitivity to depth to the water table was tested, two model configurations were used; one with depth to water table = 5.0 feet, and the other with depth to water table = 300.0 feet. In these two configurations, all other variables were set to their intermediate values (table 3).

Changes in time of travel as the result of varying each variable within its expected range (table 3) are shown in figure 4. Time of travel is most sensitive to deep percolation, organic-carbon content of the lower layer, depth to the water table, and residual moisture content. Time of travel is independent of pesticide half-life and is very insensitive to porosity and air-entry level. With all other variables set at their

intermediate values, a depth to water table of 5 feet results in the shortest time of travel.

Ranges in the fraction of pesticide remaining in water that reaches the water table are shown in figure 4. The variables to which the model is most sensitive are deep percolation (recharge), organic-carbon content of the lower layer, and pesticide half-life. The model is very insensitive to field capacity, porosity, and air-entry level. Given that the values for all other variables are intermediate values, the variables that result in the greatest fraction of pesticide remaining are deep percolation, pesticide half-life in the lower layer, depth to the water table, and residual moisture content.

Results of sensitivity analyses are dependent on the values selected as "intermediate" for the variables. To show this, the sensitivity analysis was rerun to represent conditions in a subregion where depth to the water table is generally much less than it is in the Midwestern United States as a whole. The ranges in time of travel in the unsaturated zone are shown in figure 5 when the value selected as intermediate for depth to the water table is set at 15 feet, instead of the previous 100 feet, and the expected range is 5 to 30 feet. Figure 5 also shows the ranges in fraction of pesticide remaining in water reaching the water table, in this same situation. Results show a reduced sensitivity to organic-carbon content of the lower layer, pesticide half-life in the lower layer, and residual moisture content.

**Table 3. Expected intermediate values and ranges of values for selected variables used in sensitivity analyses**

Variables	Intermediate values	Range of values		
Infiltration at land surface (inches per year)	40.0	10.0	-	70.0
Deep percolation (inches per year)	10.0	0.01	-	20.0
Depth to water table (feet)	100.0	5.0	-	300.0
Thickness of root zone (feet)	3.0	1.0	-	6.0
Residual moisture content (dimensionless)	.12	0.02	-	0.3
Field capacity (dimensionless)	.20	0.10	-	0.35
Porosity (dimensionless)	.40	0.15	-	0.60
Air-entry level (feet)	1.0	0.10	-	8.0
Organic-carbon partition coefficient (cubic feet per pound)	2.56	0.8	-	4.0
Organic-carbon content, upper layer (percent)	.8	0.1	-	5.0
Organic-carbon content, lower layer (percent)	0	0	-	0.5
Pesticide half-life in upper layer (days)	182.5	10.0	-	365.0
Pesticide half-life in lower layer (days)	365.0	60.0	-	1,825.0

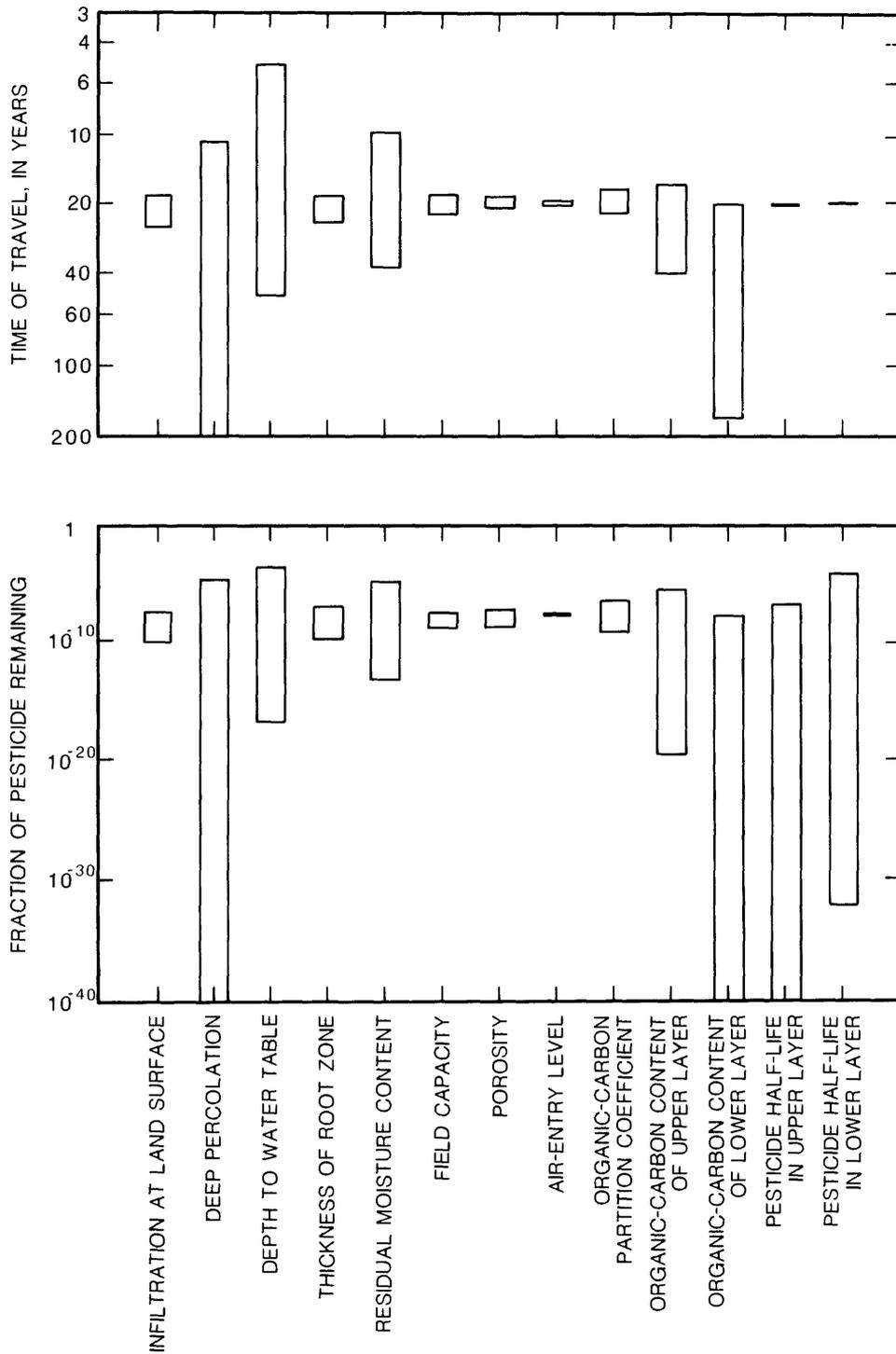
The results of sensitivity analysis are biased by the use of intermediate values and the independent variation of model variables. Furthermore, results of sensitivity analyses do not demonstrate susceptibility to ground-water contamination under extreme conditions that may exist at some localities. The overlapping of several conditions that favor ground-water contamination may cause contamination to become more certain.

## SUMMARY

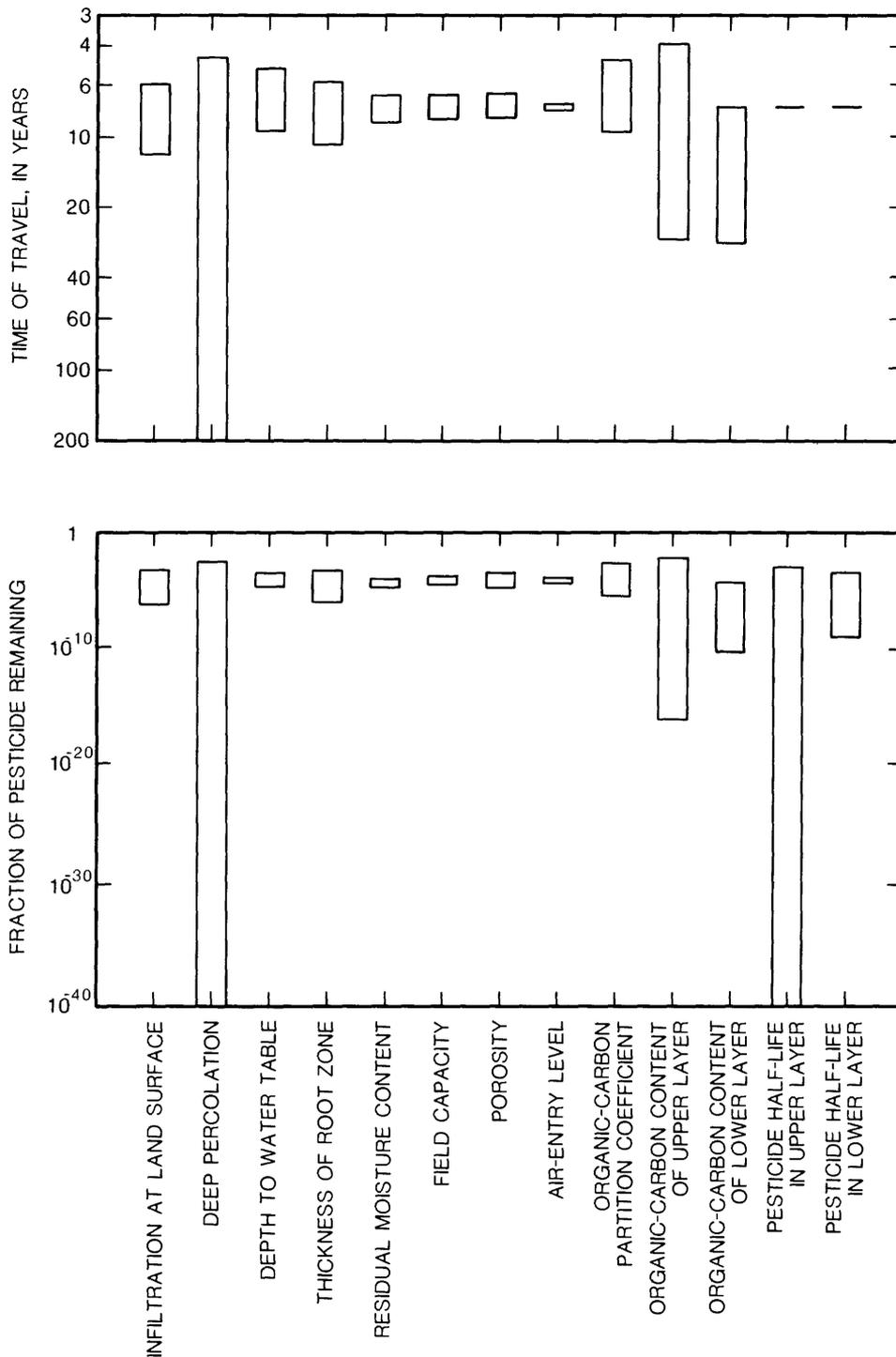
The model described here is intended to be used for regional assessments of susceptibility of ground water to nonpoint-source pesticide

contamination. It is useful provided the user is aware of the assumptions upon which it is based. These assumptions may limit the applicability of the model results, but limitations become less significant if model results are used in a comparative sense.

Advantages of the model described herein include the simplicity of data input and output and the executability of the program on a variety of computers. The model code, written in FORTRAN-77, can be obtained from the authors. Disadvantages of the model include the assumption of steady-state conditions and no consideration of nonaqueous-phase pesticide transport.



**Figure 4.** Ranges in time of pesticide travel through unsaturated zone and fraction of pesticide remaining in water that reaches water table as a result of modifying value of each variable within its expected range while maintaining all other variables at their intermediate values.



**Figure 5.** Ranges in time of pesticide travel through unsaturated zone and fraction of pesticide in water that reaches water table as a result of modifying value of each variable within its expected range while maintaining all other variables at their intermediate values except depth to water table, for which the expected range has been changed to 5 to 30 feet and the intermediate value changed to 15 feet.

The model calculates time of travel of surface-applied pesticides and fraction of pesticide remaining as functions of depth in the unsaturated zone. Results from the model can help rank, by order of importance, the variables that affect pesticide occurrence among the variables evaluated by the model, and thereby aid in interpreting measured ground-water quality.

Results of the use of the model to simulate pesticide transport in the unsaturated zone indicate that, of the 13 variables tested, those to which the model is most sensitive are deep percolation, organic-carbon content in the lower part of the unsaturated zone, pesticide half-life, and depth to the water table, using values of variables that represent the agricultural region of the Midwestern United States. Any assessment in this region of nonpoint-source ground-water contamination by pesticides that originate at land surface requires that these variables be accurately quantified.

Results of sensitivity analyses are dependent on the values selected as intermediate for the model variables. For example, if a reduced value for intermediate depth to the water table is used, the sensitivity to organic-carbon content and pesticide half-life in the lower part of the unsaturated zone is reduced.

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