



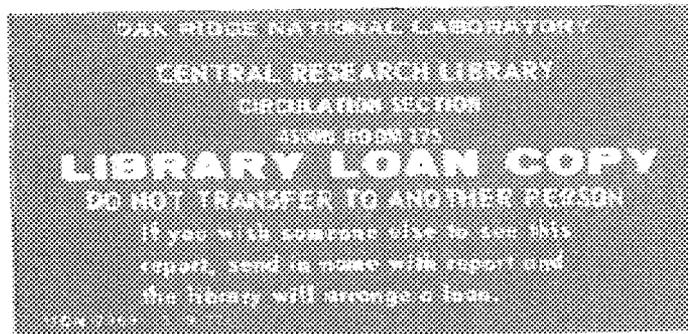
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MARTIN MARIETTA

**Qualitative Validation of
Pollutant Transport Components of an
Unsaturated Soil Zone Model (SESOL)**

D. M. Hetrick
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R. S. Kinerson



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Health and Safety Research Division

QUALITATIVE VALIDATION OF POLLUTANT TRANSPORT COMPONENTS
OF AN UNSATURATED SOIL ZONE MODEL (SESOIL)

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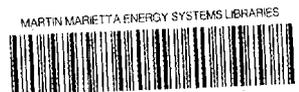
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ABSTRACT

Model predictions of a revised version of the soil compartment model SESOIL are compared with empirical measurements of pollutant transport in soil. A description of SESOIL is given, and modifications to the model are presented. Comparisons are performed using data from a laboratory soil column study involving six chemicals (dicamba, 2,4-dichlorophenoxyacetic acid, atrazine, diazinon, pentachlorophenol, and lindane) and data from three field studies involving the transport of aldicarb and atrazine. Model performance and limitations are discussed.

1. INTRODUCTION

Pollutant transport and transformation in the unsaturated soil zone are complex processes affected by soil and hydrogeological properties, climatic conditions, and chemical characteristics. In recent years, research has produced numerous models that predict fate and transport of pollutants through the soil.¹⁻⁴ However, relatively little has been done to compare or validate results of model predictions with field measurements of pollutant transport.

The SEasonal SOIL model SESOIL,² a code developed for the U.S. Environmental Protection Agency (EPA) Office of Toxic Substances (OTS), estimates concentrations of pollutants in the soil following introduction via direct application and/or interaction with other media (i.e., deposition from air). The soil hydrology submodel of SESOIL has been evaluated by Hetrick et al.,^{5,6} and a number of other studies have been conducted on the SESOIL model including sensitivity analysis, comparison with other models, and some limited comparisons with measured data.⁷⁻¹⁰ The purpose of this paper is to study the performance of the pollutant transport cycle submodel of an improved version of SESOIL. The comprehensive evaluation of SESOIL performed by Watson and Brown¹¹ uncovered numerous deficiencies in the model, and thus the SESOIL code has been extensively modified at Oak Ridge National Laboratory (ORNL) to enhance its capabilities. This paper includes a brief description of the processes simulated in SESOIL and documents the modifications made to the model.

We will evaluate the performance of SESOIL by comparing its predictions with a variety of published experimental data for pollutant transport in the soil column. Data sets chosen for comparison were a laboratory study by Melancon et al.¹⁰ involving six organic chemicals (dicamba, 2,4-dichlorophenoxyacetic acid, atrazine, diazinon, pentachlorophenol, and lindane), and three field experiments, two of which involved the movement of aldicarb in field plots^{12,13} and the third investigated the transport

of atrazine in a small watershed.¹⁴ In each case, unknown hydrologic parameters were calibrated until components of the hydrologic cycle of the model compared well with limited measurements; predictions of components of the pollutant cycle were then compared with available data. Conclusions regarding SESOIL's performance and limitations are presented.

SESOIL is incorporated into EPA's Graphical Exposure Modeling System (GEMS), a system developed to support integrated exposure analysis at OTS.¹⁵ (The model is maintained by OTS of EPA; interested users should contact R. S. Kinerson, OTS, Washington, D.C.)

2. SESOIL MODEL DESCRIPTION

The SESOIL model² estimates pollutant concentrations in the soil profile following introduction via direct application and/or interaction with other media (i.e., deposition from air). The model defines the soil compartment as a soil column extending from the ground surface through the unsaturated zone and to the upper level of the saturated soil zone. Processes simulated in SESOIL are categorized in three cycles - the hydrologic cycle, sediment cycle, and pollutant cycle. Each of the three cycles are separate submodels in the SESOIL code. The hydrologic cycle includes rainfall, surface runoff, infiltration, soil water content, evapotranspiration, and groundwater runoff. The sediment cycle includes sediment washload as a result of rainstorms (i.e., soil erosion that results from surface runoff). The pollutant cycle includes convective transport, volatilization, adsorption/desorption, and degradation/decay. The SESOIL model does not address pollutant movement in saturated groundwater.

SESOIL is considered to be a screening-level model and thus data requirements are not extensive, utilizing a minimum of soil and chemical parameters and monthly or seasonal meteorological values as input. Output of the SESOIL model includes pollutant concentrations at various soil depths and pollutant loss from the unsaturated soil zone in terms of surface runoff, percolation to groundwater, volatilization, and degradation. Complete descriptions of the SESOIL algorithms can be found in Bonazountas and Wagner.² The three major cycles are now summarized. More details are given for the pollutant cycle since descriptions of the SESOIL algorithms for this cycle have not been published in the open literature.

2.1 HYDROLOGIC CYCLE

The hydrologic cycle of SESOIL employs the water balance dynamics theory of Eagleson,¹⁶ which couples the climate and soil systems through statistically based modeling. The cycle includes rainfall, surface runoff, infiltration, soil water content, evapotranspiration, and groundwater runoff. SESOIL's hydrologic submodel defines the soil compartment as a soil column extending from the ground surface through the unsaturated zone and to the upper level of the saturated soil zone. Thus, in the hydrologic cycle the entire unsaturated zone is conceptualized as a single layer and the prediction for soil water content is to be considered as an average value for the entire unsaturated zone. The cycle is

thoroughly described by Eagleson¹⁶ and is summarized by Bonazountas and Wagner² and Hetrick et al.⁶ SESOIL model predictions of watershed hydrologic components have been compared with those of the more data-intensive terrestrial ecosystem hydrology model AGTEHM¹² as well as to empirical measurements at a deciduous forest stand watershed and a grassland watershed.⁶ The model was found to be a good predictor of annual values of infiltration, evapotranspiration, surface runoff, and groundwater runoff.

2.2 SEDIMENT CYCLE

The sediment cycle of SESOIL employs the washload yield model EROS, which is part of the CREAMS model.^{18,19} The erosion theory used in EROS has been summarized by Knisel et al.²⁰ and Bonazountas and Wagner.² The erosion component considers the basic processes of soil detachment, transport, and deposition. Options for annual and monthly simulation of sediment washload are included. The annual option is based on the Universal Soil Loss Equation of Wischmeier and Smith²¹; the monthly option, however, uses modifications of procedures developed by Foster et al.¹⁰ for the CREAMS model. The EROS submodel was not used in this analysis since the coupled SESOIL/EROS models have not been thoroughly tested or validated. Thus, there was no accounting for pollutant transport with sediment in this work.

2.3 POLLUTANT CYCLE

The SESOIL model predicts annual or monthly pollutant concentrations in the soil water or liquid phase ($\mu\text{g/mL}$), soil air or gaseous phase ($\mu\text{g/mL}$), and adsorbed or solid phase ($\mu\text{g/g}$) in up to four major soil layers. (Note that recent modifications to SESOIL now allow up to 10 sublayers in each of the four soil layers. See the discussion in the next section.) The amount of pollutant lost from the unsaturated soil zones is provided in terms of $\mu\text{g/cm}^2$ lost via surface runoff, percolation to groundwater, volatilization, and degradation. Complete descriptions of the SESOIL algorithms can be found in Bonazountas and Wagner² and are based on the following mass balance equation:

$$M_{\text{orig}}(t-1) + M_{\text{input}}(t) = M_{\text{trans}}(t) + M_{\text{rem}}(t) + M_{\text{out}}(t), \quad (1)$$

where

- $M_{\text{orig}}(t-1)$ = pollutant mass originally in the soil layer at time $t-1$ ($\mu\text{g/cm}^2$),
- $M_{\text{input}}(t)$ = pollutant mass introduced into the soil layer during a time step ($\mu\text{g/cm}^2$),
- $M_{\text{trans}}(t)$ = pollutant mass transformation within the soil layer during the time step ($\mu\text{g/cm}^2$),
- $M_{\text{rem}}(t)$ = remaining pollutant mass in the soil layer at time t ($\mu\text{g/cm}^2$),
- $M_{\text{out}}(t)$ = pollutant mass transported out of the soil layer during the time step ($\mu\text{g/cm}^2$).

The transport/transformation of the pollutant in each soil layer of SESOIL depends on the pollutant partitioning among the three phases. The partitioning is a function of chemical-specific partition coefficients and rate constants. In SESOIL, the three phases are assumed to be in equilibrium at all times. Thus, once the concentration in one phase is known, the concentrations in the other phases can be calculated. The pollutant cycle of SESOIL is based on the chemical concentration in the soil water. The concentration in the soil air is calculated via the modified Henry's law,

$$c_{sa} = cH/[R(T + 273)], \quad (2)$$

where

- c_{sa} = pollutant concentration in soil air ($\mu\text{g/mL}$),
- c = pollutant concentration in soil water ($\mu\text{g/mL}$),
- H = Henry's law constant ($\text{m}^3 \text{atm/mol}$),
- R = gas constant [$8.2 \times 10^{-5} \text{ m}^3 \text{atm}/(\text{mol K})$],
- T = soil temperature ($^{\circ}\text{C}$).

The adsorption equation used in SESOIL for the soil phase is represented by the Freundlich isotherm

$$s = K_d c^{1/n}, \quad (3)$$

where

- s = pollutant adsorbed concentration ($\mu\text{g/g}$),
- K_d = pollutant partitioning coefficient ($\mu\text{g/g}/(\mu\text{g/mL})$),
- c = pollutant concentration in soil water ($\mu\text{g/mL}$),
- n = Freundlich exponent.

The total concentration of the pollutant in the soil is computed as

$$c_o = (f-\theta)c_{sa} + \theta c + \rho_b s, \quad (4)$$

where

- c_o = overall (total) pollutant concentration ($\mu\text{g/cm}^3$),
- f = total soil porosity (mL/mL),
- θ = soil water content (mL/mL),
- $f-\theta$ = f_a , the air-filled porosity (mL/mL),
- ρ_b = soil bulk density (g/cm^3).

In SESOIL, each soil layer is considered as a compartment with a set volume and the total soil column is treated as a series of interconnected layers. Each layer has its own mass balance equation [Eq. (1)] and can receive and release pollutant to and from adjacent layers. The individual fate processes that compose the SESOIL mass balance equations (e.g., volatilization, degradation) are functions of the pollutant concentration in the soil water of each zone and a variety of rate (first-order), partitioning, and other constants.

Some of the concentration terms in SESOIL are nonlinear and thus an iterative solution procedure is used to solve the system. The pollutant

cycle equations are formulated on a monthly basis (an annual option is available) and results are output for each month simulated. However, the equations are written with an explicit time step and to account for the dynamic processes in the model more accurately, a time step of 1 d is used. The monthly output represents the summation of results from each day.

3. SESOIL MODEL MODIFICATIONS

Watson and Brown¹¹ tested and evaluated the SESOIL model and found numerous deficiencies. The code has subsequently been extensively modified to correct many of these deficiencies. These modifications are now discussed.

3.1 CHEMICAL RETARDATION FACTOR

In SESOIL, a convective velocity is used to determine the depth the pollutant will reach during a time step. The depth d is calculated as

$$d = J_w t_c / \theta, \quad (5)$$

where

$$\begin{aligned} J_w &= \text{water flux (cm/s),} \\ t_c &= \text{convection time (s),} \\ \theta &= \text{soil water content (cm}^3\text{/cm}^3\text{).} \end{aligned}$$

Equation (5) allows all chemicals to reach groundwater at the same time, irrespective of their chemical sorption characteristics. Equation (5) has been replaced with

$$d = J_w t_c / \{ \theta + \rho_b K_d + f_a H / [R (T + 273)] \}, \quad (6)$$

which is the depth reached by a chemical with a linear equilibrium partitioning between its vapor, liquid, and adsorbed phases.²²

3.2 SUBLAYERS

The pollutant cycle of the SESOIL model allows up to four major soil layers (or compartments), each with a defined depth and thus a set volume. When a chemical enters a layer it is instantaneously distributed uniformly throughout the whole layer and one concentration is computed for that compartment. Therefore, the larger the compartment (or layer), the smaller the pollutant concentration. For these reasons, the SESOIL model was discretized so that each of the four major soil layers can have up to ten sublayers, each having the same soil properties as the major layer in which they reside.

3.3 VOLATILIZATION

The volatilization algorithm was modified so that if the chemical is in the second or lower layer, and the concentration in that layer is greater than the layer above it, then the chemical will diffuse into the upper

layer rather than volatilize directly into the atmosphere as before. The new volatilization model is still based on a model of Farmer et al.²³ and Millington and Quirk²⁴ and is a discretized version of Fick's first law over space, assuming vapor phase diffusion as the rate controlling process. The volatilization flux through the soil J_a ($\mu\text{g}/\text{cm}^2\text{s}$) is described as

$$J_a = -D_a(f_a^{10/3}/f^2)dC_{sa}/dx, \quad (7)$$

where D_a is the vapor diffusion coefficient of the compound in air (cm^2/s).

3.4 PURE CHEMICAL PHASE

A pure chemical phase was added to the model so that the simulated pollutant concentration in the dissolved (soil water) phase can not exceed the solubility of the chemical. If during solution of the mass balance equation for any one layer, the dissolved concentration exceeds the solubility of the chemical, the iteration is stopped and the solubility is used as the dissolved concentration. The adsorbed and soil-air concentrations are calculated using the chemical partitioning equations as before [Eqs. (2) and (3)]. To achieve mass balance the excess chemical is assumed to be in the pure phase. Transport of the pure phase is not considered, but the mass of the chemical in the pure phase is used as input to that layer in the next time step. Simulation continues until the pure phase eventually disappears due to infiltration, degradation, and other model processes.

3.5 SOIL TEMPERATURE

The earlier version of the SESOIL model assumed that soil temperature was equal to air temperature. The model has been modified to predict soil temperature from air temperature:²⁵

Summer:	$Y = 16.115 + 0.856 X,$	
Fall:	$Y = 1.578 + 1.023 X,$	(8)
Winter:	$Y = 15.322 + 0.656 X,$	
Spring:	$Y = 0.179 + 1.052 X,$	

where Y is the mean monthly soil temperature ($^{\circ}\text{F}$), and X is the mean monthly air temperature ($^{\circ}\text{F}$). These regression equations are very crude and not depth dependent; however; further complexity is not warranted since soil temperature is used only in Eq. (2) and does not significantly affect results.

3.6 MISCELLANEOUS MODIFICATIONS

Previously, SESOIL took a monthly input pollutant load, divided it by the number of time steps per month, and added that amount to the soil column each time step during the month. A new option was added to the input capabilities of SESOIL that allows the total chemical mass to be

loaded into the soil column at the beginning of the first time step of any month. Thus, SESOIL now has the capability of handling a spill loading.

Several coding errors were found and corrected while thoroughly testing and verifying the pollutant cycle algorithms in SESOIL. Also, the subroutine that prints the results from SESOIL was rewritten not only to be more efficient but so that the output would be more readable.

4. VALIDATION DESIGN

The new version of SESOIL was evaluated by comparing its predictions with a variety of published experimental data. These data include transit time through the soil column, the amount of pollutant in daily effluent samples, the time-dependent depth distribution of the pollutant, and the mass balance at any time (cumulative mass in soil, in leachate, and in the degradation, runoff, and volatilization components). The sum of the mass balance components should equal the amount of chemical applied initially. The data used in this evaluation are now summarized.

4.1 LABORATORY STUDY

Melancon et al.¹⁰ filled four 2-m columns (59.4 cm ID) with sandy soil, applied a chemical to the surface, and watered each column for 30 d. A total of 285 cm of water was added to each column during that time. (This value is roughly an order of magnitude higher infiltration than normally expected from rainfall.) The quantity of chemical leachate was recorded daily. Thirty days after application of the chemical to the surface, the experiment was stopped; each column was broken down, and the amount of pollutant remaining in every 5-cm section of the column was measured. Six organic chemicals were studied: 2,4-dichlorophenoxyacetic acid (2,4-D), atrazine, diazinon, dicamba, lindane, and pentachlorophenol (PCP). The values for sorption, degradation rate, and the Freundlich exponent were determined in the laboratory by Lopez-Avila et al.^{26,27} These chemicals are commonly used in agriculture. They cover a wide range of adsorption coefficients (see Table 1) and thus constitute a reasonably thorough test of any modeling program.

Melancon et al.¹⁰ compared the results of their soil column studies with the predictions of three soil modeling programs: PESTAN,⁴ PRZM,³ and the old version of SESOIL.² Note that daily leachate data are not provided by SESOIL because one would not typically want daily output from a screening-level model. Thus the old version of SESOIL was not tested in this regard. Melancon et al.¹⁰ found that the values they measured for various model input parameters, such as the degradation rate and the adsorption coefficient, differed markedly from values published in the literature. Frequently, users of transport models are forced to use data from some published source (based upon general soil type) since little site-specific information is available. Therefore, Melancon et al.¹⁰ ran each model twice, once with input parameters obtained from the literature and once with their measured input parameters, to see how the differences affected the results.

Table 1. Summary of rate constants and other model input data used in SESOIL based on literature values and laboratory measurements

	Dicamba	2,4-D	Atrazine	Diazinon	PCP	Lindane
Adsorption coefficient K_d (cm^3/g)						
Literature measured	0.002	0.021	0.168	0.678	0.945	2.625
	0.120	0.140	0.493	1.632	3.341	3.530
Solubility (mg/L) ^a	4500	900	33	40	14	7.8
Degradation rate (d^{-1})						
Literature measured	0.065	0.040	0.010	0.015	0.033	0.005
	0.009	0.140	0.009	0.032	0.025	0.032
Freundlich exponent						
Literature measured	0.850	1.330	1.140	1.000	2.380	1.020
	1.120	0.960	1.360	1.110	1.210	1.230
Henry's Law constant ^a	1.29E-9	1.939E-10	7.29E-9	1.40E-6	2.80E-6	7.80E-6
Neutral hydrolysis rate constant ^a	0	0	0	4.30E-8	0	0
Acid hydrolysis rate constant ^a	0	0	0	2.10E-2	0	0
Basic hydrolysis rate constant ^a	0	0	0	5.30E-3	0	0
Molecular weight	221.04	221.04	216.06	304.36	266.35	290.85
Diffusion coefficient in air (cm^2/s) ^a	6.05E-2	6.05E-2	5.93E-2	5.54E-2	5.92E-2	5.58E-2

Table 1 (continued)

<u>Soil parameters</u>	Bulk density (g/cm ³)	Porosity (cm ³ /cm ³)	Organic carbon (%)	Intrinsic perm. (cm ²)	Disconn. index c
Literature	1.57	0.35	a	1.1E-7	4.6
measured	1.38	a	0.105	a	a

<u>Environmental parameters</u>	Temp. (°C)	Relative humid. (%)	Evap. (cm/d)	Albedo (-)	Watering rate (cm/d)	Cloud cover (frac)
Literature	29.6	42.0	1.130	0.250	9.67	0.32
measured	26.7	66.7	0.189	0.220	9.67	0.32

^aSame values used for both literature and measured runs.

Source: S. M. Melancon, J. E. Pollard, and S. C. Hern, "Evaluation of SESOIL, PRZM, and PESTAN in a Laboratory Column Leaching Experiment." *Environ. Topical. Chem.* 5(10), 865-78 (1986).

For this study, the input parameters were obtained from Melancon et al.¹⁰ and tested first with the old version of SESOIL to verify their results. Testing then began on the new SESOIL version. The code was temporarily modified to print out the daily leachate so that these results could be compared with the experimental data along with the end-of-the-month distribution data. Both the measured and the literature input parameters were used (see Table 1). In order to make the hydrology of the model agree more closely with the experimental setup, the values of K1 (the soil intrinsic permeability) and c (the soil disconnectedness index) were varied to reduce the predicted surface runoff to below 1 cm/month while maintaining the predicted soil water content at about the measured value (approximately $0.125 \text{ cm}^3/\text{cm}^3$). This procedure is recommended in the SESOIL user's guide² and is discussed by Hetrick et al.⁶ in their study of the SESOIL hydrologic cycle. The parameter c is defined as the exponent relating the "wetting" or "drying" time-dependent permeability of a soil to its saturated permeability,¹⁶ and typically ranges in value from 12 for clay type soils to 3.7 for sandy soils. The same values of K1 and c were used in both the measured and the literature runs.

4.2 FIELD STUDIES

R. L. Jones and colleagues have conducted research on the movement and degradation of aldicarb residues in the unsaturated and saturated zones at a number of sites in 16 states over a period of 6 years.²⁸ We have chosen two of these sites for analysis in this paper. Laboratory and field tests were conducted to examine leaching behavior at a site located in Polk County near Lake Hamilton, Florida. This site was located in an orange grove with deep coarse sand texture which had not previously been treated with aldicarb. The laboratory and field experiments conducted in this citrus grove are described by Hornsby et al.²⁹ (1983) and model comparisons conducted with the data are reported by Jones et al.¹² Measured data used as input to SESOIL are given in Table 2. Climatic data were provided by Jones (R. L. Jones, personal communication, 1986) from the Lake Alfred Experimental Station or were taken from nearby weather stations.³⁰ Aldicarb was applied to the site on February 16, 1983, and soil samples were collected on March 4, April 6, May 3, June 15, and August 24. The SESOIL code was temporarily modified to accept the aldicarb application on February 16 and to print results on the days the soil samples were collected. Measurements included the transit time of the aldicarb within the unsaturated zone and aldicarb distributions in the soil profile. Samples were collected at approximately 30-cm intervals to a depth of 60 cm and 60-cm intervals to a depth of 420 cm. The aldicarb concentrations were observed to be highly variable but did show progression towards the groundwater table with time.

The second site chosen in this analysis is located in a vineyard 10 km southwest of Fresno, California. This site is representative of conditions in central California under which aldicarb residues are most likely to reach drinking water supplies.¹³ The soil at this site is a sandy loam with intermittent layers of silt loam at the 2- to 3-m depth and coarse sand layers below 3 m. The test plot was irrigated by flooding the wide furrows between rows of vines spaced about 3.6 m apart. Aldicarb

Table 2. Summary of rate constants and other model input data used in SESOIL for the Lake Hamilton, Florida, site^a

Chemical characteristics

Adsorption coefficient K_d ($\mu\text{g/g}/\mu\text{g/mL}$)	0.0612
Degradation rate (d^{-1})	0.0220
Solubility ($\mu\text{g/mL}$)	6000.0
Henry's Law constant ($\text{m}^3\text{-atm/mol}$)	3.3E-9
Diffusion coefficient in air (cm^2/s)	0.0600
Molecular weight (g/mol)	190.00

Soil characteristics

Soil bulk density (g/cm^3)	1.5500
Intrinsic permeability (cm^2)	2.0E-7
Disconnectedness index	3.8000
Porosity (mL/mL)	0.3500
Organic carbon content (%)	0.1700
Freundlich exponent	1.0000

^aAll other chemical and soil data needed for SESOIL and not listed above were assumed to be 0.0.

was applied at the rate of 4.46 kg ai/ha to the plot on April 11, 1984, to both sides of the vines with two shafts per side spaced 0.3 m apart, with the first shank located approximately 0.4 m away from the vines.¹³ Soil samples were taken prior to treatment and at regular intervals after treatment down to a maximum depth of 7.8 m. Downward movement of aldicarb was rapid at this site because the aldicarb was applied to the bottom of a wide furrow and the plot was essentially flood irrigated.¹³ Irrigation records were added to rainfall data for input to the SESOIL code. Other meteorological data were taken from 30-year-averaged data measured at the Fresno weather station.³⁰ Pertinent measured data used as input to SESOIL are given in Table 3.

The last field site chosen in this study is a single-field watershed located in the Southern Piedmont Conservation Research Center near Watkinsville, Georgia. This study was a joint effort of the U.S. Environmental Protection Agency and the U.S. Department of Agriculture and was designed to provide a data base for the conceptual development and testing of operational models for describing pesticide and nutrient transport from agricultural lands.¹⁴ Detailed measurements of runoff, evaporation, soil water content, and precipitation were collected from four small watersheds over a period of 3 years. Concentrations for six herbicides in surface runoff and at seven depths in the soil profile were also measured. Smith et al.¹⁴ discuss the experimental design and sampling procedures in detail.

Measurements following the application of atrazine on one of the watersheds, the "P2 Watershed," were selected for purposes of testing SESOIL. This watershed is 1.29 hectares in size with variable soils ranging from a sandy clay loam to loam, the major soil being a Cecil sandy loam. The depth to the groundwater table is about 12 m.

Over three planting seasons, detailed monitoring of hydrological and chemical transport was conducted. Most of the data needed as input to SESOIL were obtained from Smith et al.¹⁴. Additional weather data were obtained from NOAA records collected at Athens, Georgia. Table 4 lists the day and rate of atrazine application for each of the 3 years. Pollutant cycle parameters used as input to SESOIL are listed in Table 5.

5. RESULTS AND DISCUSSION

Comparison of the distribution of organic chemicals present in soil with model predictions can be accomplished in a variety of ways.³¹ Descriptive and statistical methodologies used for comparing model simulations with observations will be dependent on the characteristics of the observed and simulated data sets. Distribution of observed and predicted data sets may be so different that statistical testing of the data may yield no more information than simple graphical presentations or tabular comparisons would provide. Even though it is recognized that statistical techniques exist for testing two data sets for differences or similarities, qualitative rather than quantitative statements will be made in the following sections. We stress that model validation is a continuing process, because no model is ever completely validated. The work presented here is an initial effort to validate several components of the pollutant cycle in SESOIL.

Table 3. Summary of rate constants and other model input data used in SESOIL for the Fresno, California, site^a

Chemical characteristics

Adsorption coefficient K_d ($\mu\text{g/g}/\mu\text{g/mL}$)	0-30 cm	0.2840
	30-60 cm	0.0630
	>60 cm	0.0320
Degradation rate (d^{-1})		0.0220
Solubility ($\mu\text{g/mL}$)		6000.0
Henry's Law constant ($\text{m}^3\text{-atm/mol}$)		3.3E-9
Diffusion coefficient in air (cm^2/s)		0.0600
Molecular weight (g/mol)		190.00

Soil characteristics

Soil bulk density (g/cm^3)		1.5500
Intrinsic permeability (cm^2)		1.8E-8
Disconnectedness index		4.8000
Porosity (mL/mL)		0.3500
Organic carbon content (%)	0-30 cm	0.9000
	30-60 cm	0.2000
	>60 cm	0.1000
Freundlich exponent		1.0000

^aAll other chemical and soil data needed for SESOIL and not listed above were assumed to be 0.0.

Table 4. Atrazine application rates and dates at the Watkinsville, Georgia, site

Year	Date	Rate ($\mu\text{g/cm}^2$)
1973	May 11	33.6
1974	April 29	38.1
1975	May 21	15.4

Table 5. Summary of rate constants and other model input data used in SESOIL for the Watkinsville, Georgia, site^a

Chemical characteristics

Adsorption coefficient, K_d ($\mu\text{g/g}/\mu\text{g/mL}$)	0.0800
Degradation rate (d^{-1})	0.0400
Solubility ($\mu\text{g/mL}$)	33.000
Henry's Law constant ($\text{m}^3\text{-atm/mol}$)	7.3E-9
Diffusion coefficient in air (cm^2/s)	0.0593
Molecular weight (g/mol)	216.06

Soil characteristics

Soil bulk density (g/cm^3)	1.6000
Intrinsic permeability (cm^2)	3.E-10
Disconnectedness index	7.0000
Porosity (mL/mL)	0.4800
Organic carbon content (%)	0.1050
Freundlich exponent	1.0000

^aAll other chemical and soil data needed for SESOIL and not listed above were assumed to be 0.0.

5.1 LABORATORY STUDY

The results of the modified SESOIL were found to agree more closely with the experimental data than the old SESOIL version (see Melancon et al., 1986).¹⁰ Using a chemical retardation factor in SESOIL to control chemical movement in the soil produces adequate results as can be seen in Table 6. The breakthrough days (days in which the chemicals appeared at bottom of soil column) predicted by SESOIL using the measured input parameters were generally quite close to the actual breakthrough days (see Table 6); at worst there was a difference of 5 d. The advantage of using the measured input parameters rather than those from the literature is quite apparent in this case. The best prediction using literature values disagrees by 3 d; the worst disagrees by 14 d. In all cases the results of SESOIL predicted that the pollutant would reach the bottom of the soil column faster than the measurements showed.

The comparison of SESOIL's predictions to the experimental measurements of the mass balance after 30 d is shown in Table 7. For comparison, results from the PESTAN and PRZM models are given also.¹⁰ All predicted values from runs with the measured input parameters except those for atrazine are within a factor of 2 of the experimental values. All three models predicted the bulk of the chemical atrazine would leach through the columns more quickly than was actually observed in the experiments.

In comparing SESOIL results using measured input parameters vs literature-derived input parameters, it is clear from Table 7 that the match between model predictions and observed data improved for 2,4-D, atrazine, and diazinon. However, model predictions did not improve for PCP and lindane, the two chemicals with the highest adsorption coefficients, or for dicamba which had the lowest adsorption coefficient of the chemicals studied. Results from the PRZM model were very similar to those from SESOIL for these three chemicals.

SESOIL results for the total chemical concentration in soil vs depth (at the end of 30 d) are compared graphically to observations from the four soil columns in Fig. 1, while the predicted distributions of the amount of pollutant in the leachate versus time are compared to the measurements in Fig. 2. Note that atrazine was the only chemical that was found in both leachate and soil samples from the actual test columns. The darkened lines in the figures show SESOIL results using measured input data, the dashed lines indicate results using literature input values, and the light lines are the measurements from the four soil columns. These figures show that there was a trend for SESOIL to more closely approximate observed chemical peak location, height, and distribution when measured rate information rather than literature-derived values were used. This situation was not the case before when using the old SESOIL code that allowed only four layers between the surface and groundwater. The predictions using the previous SESOIL version did not improve with the use of measured rate constant information.¹⁰ This study shows (1) the importance of discretizing the SESOIL model to become essentially an n-layered model, and (2) the effect of using a chemical retardation factor.

Table 6. Day of chemical breakthrough in effluent samples and SESOIL results

	<u>Breakthrough days</u>
<u>2,4-D</u>	
Measured:	10, 12, 11, 11 (4 soil columns)
SESOIL Results:	
Measured Input Data:	7
Literature Input Data:	4
<u>Atrazine</u>	
Measured:	21, 21, 23, 23
SESOIL Results:	
Measured Input Data:	18
Literature Input Data:	9
<u>Dicamba</u>	
Measured:	6, 7, 7, 7
SESOIL Results:	
Measured Input Data:	7
Literature Input Data:	3
<u>Diazinon</u>	
Measured:	>30 d
SESOIL Results:	
Measured Input Data:	>30 d
Literature Input Data:	27

^aMeasurements nor SESOIL results "broke through" the columns within 30 days for Lindane or PCP.

Table 7. Mass balance calculations for measured chemical data (average from 4 columns) vs PESTAN, PRZM, and SESOIL model predictions, showing cumulative mass (mg) in soil, leachate, and degradation components on day 30 (based on 250.5-mg initial loading)

	Literature runs			Measured runs		
	Soil	Leachate	Degradation	Soil	Leachate	Degradation
<u>Dicamba</u>						
PESTAN	-	22.0	228.4	-	169.6	80.5
PRZM	-	214.9	35.6	-	233.9	16.5
SESOIL	-	199.9	50.6	0.0009	234.0	16.5
Meas.	-	216.7(+96.6) ^a	33.8 ^a	-	216.7(+96.6) ^a	33.8 ^b
<u>2,4-D</u>						
PESTAN	-	82.8	167.8	-	4.3	246.3
PRZM	-	221.0	29.4	-	81.5	168.9
SESOIL	0.0003	210.8	39.7	-	80.9	169.6
Meas.	-	48.7(+24.1)	201.8 ^b	-	48.7(+24.1)	201.8 ^a
<u>Atrazine</u>						
PESTAN	-	242.4	8.1	2.0	189.5	58.9
PRZM	-	231.3	29.1	4.8	210.0	35.5
SESOIL	0.057	226.2	224.3	24.3	183.2	42.9
Meas.	94.8(+22.2) ^a	4.0(+2.6) ^a	151.7 ^b	94.8(+22.2) ^a	4.0(+2.6) ^a	151.7 ^b
<u>Diazinon</u>						
PESTAN	-	246.5	7.0	152.2	-	98.2
PRZM	4.8	18.7	226.9	96.7	0.9	152.8
SESOIL	87.6	56.6	106.3	86.2	-	164.3
Meas.	47.2(+18.2) ^a	-	203.3 ^a	47.2(+18.2) ^a	-	203.3 ^a
<u>PCP</u>						
PESTAN	105.0	-	157.4	203.0	-	47.2
PRZM	71.1	29.1	150.2	120.4	-	130.0
SESOIL	98.7	-	151.8	120.3	-	130.2
Meas.	76.2(+38.5) ^a	-	174.3 ^b	76.2(+38.5)	-	174.3 ^b
<u>Lindane</u>						
PESTAN	238.3	-	13.2	192.6	-	57.4
PRZM	215.6	-	34.8	96.4	-	154.0
SESOIL	185.2	-	65.3	96.2	-	154.3
Meas.	179.6(+25.4) ^a	-	70.9 ^b	179.6(+25.4) ^a	-	70.9 ^b

^aNumbers in parentheses show 95% confidence limits about the average measured data (p = 0.05).

^bChemical unaccounted for in either the observed effluent or soil samples is assumed lost to degradation.

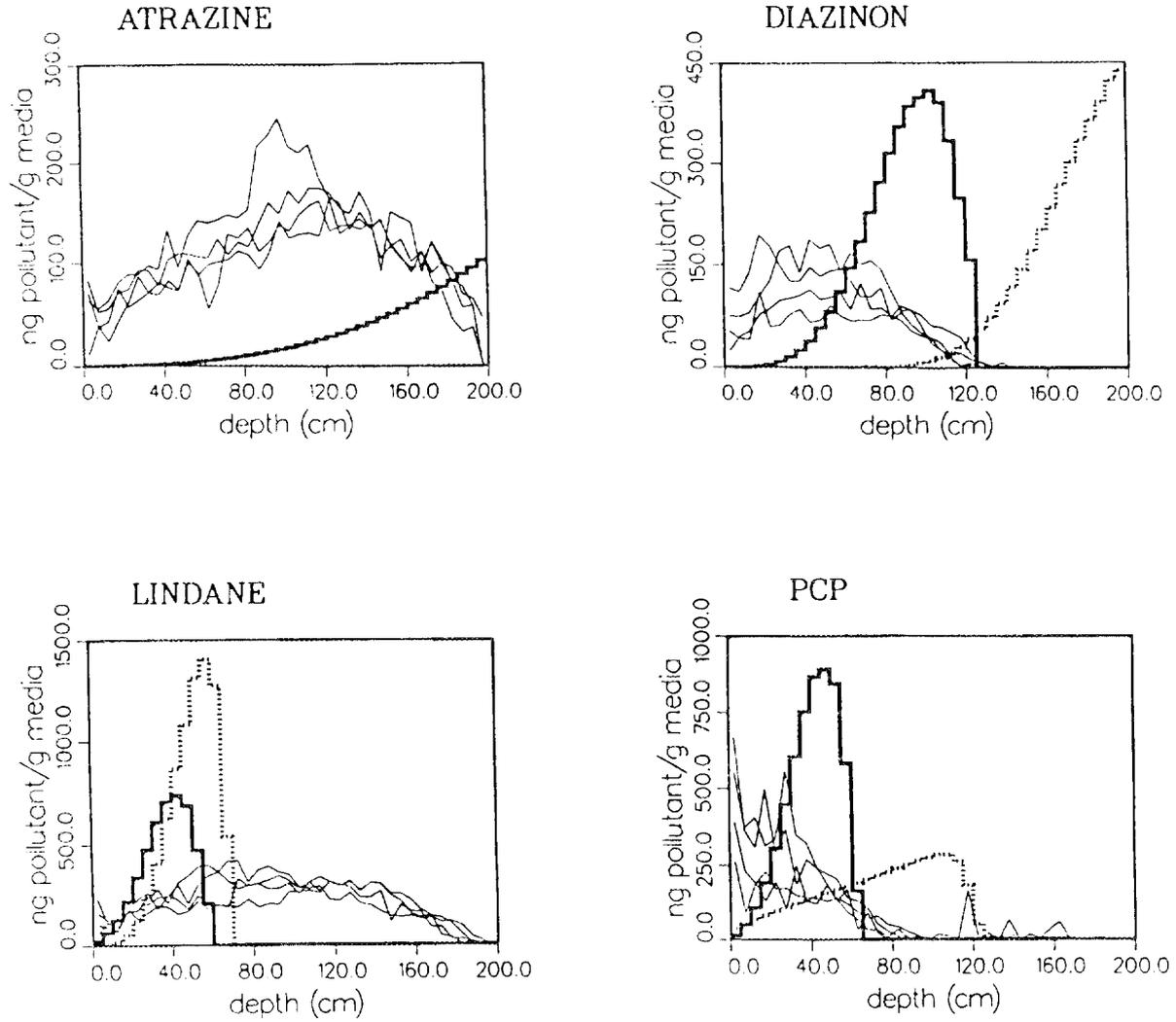


Fig. 1. Results of SESOIL "Measured" (dark line) and "Literature" (dashed line) simulations compared with column data (light lines) for atrazine, diazinon, and PCP.

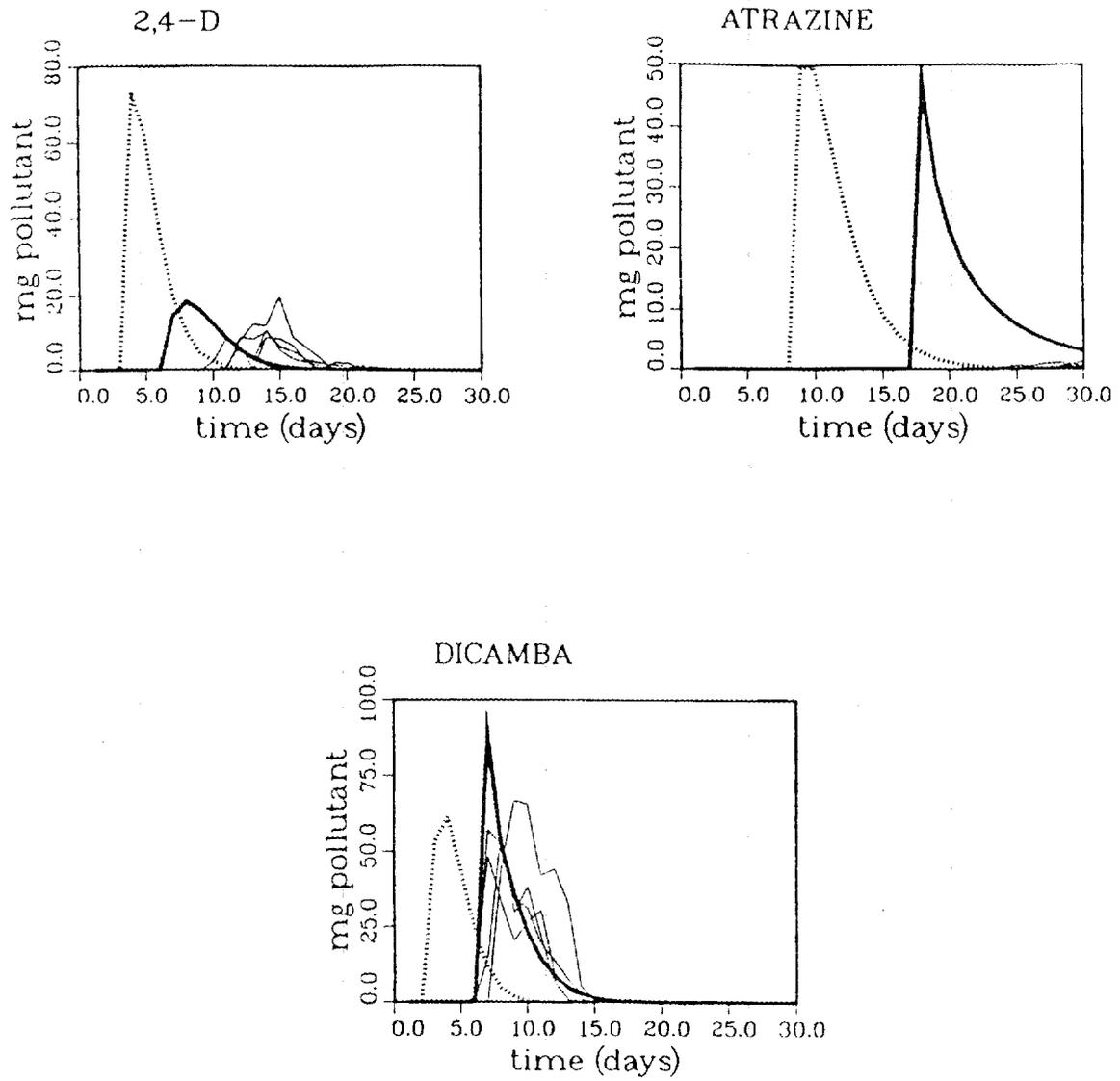


Fig. 2. Results of SESOIL "Measured" (dark line) and "Literature" (dashed line) simulations compared with column data (light lines) for 2,4-D, atrazine, and dicamba.

5.2 FIELD STUDIES

For each of the three field studies in this analysis, the SESOIL hydrologic predictions were calibrated until results compared well with measurements. Ideally, we would like to have the necessary data so that optimization is not required, but unfortunately this situation is rare. The only hydrologic measurements available at the Lake Hamilton site were for soil water. Thus, SESOIL predictions for soil water were calibrated to the measurements by optimizing the input values for the disconnectedness index c and soil porosity f ,² as all other input parameters needed for SESOIL were known.^{28,12} Final SESOIL predictions vs measured vertically averaged soil water contents are shown in Fig. 3. The agreement is reasonable because the soil texture at Lake Hamilton varies considerably with depth and the hydrologic submodel of SESOIL assumes a homogeneous soil column.

The movement of the concentration peak as predicted by SESOIL is compared with the measured values for the deepest penetration of aldicarb residues in Fig. 4. Even though the measured data for the degradation rate and the adsorption coefficient varied with depth,²³ constant values were used in the SESOIL simulation (see Table 2). This was felt to be reasonable considering the variability in the measured field data.²⁹ Note that these results (Fig. 4) would differ considerably if depth-dependent adsorption coefficients were used. The fair agreement is a confirmation of the average adsorption coefficient used rather than how well the model predicts actual concentration profiles. Comparison of the predicted leaching depths to measurements is an important test of model performance because knowledge of the leading edge of a pollutant is important in assessing the occurrence in drinking water.

The predicted amount of aldicarb remaining in the upper 3 m of the unsaturated zone at the Lake Hamilton site is compared to measured data in Fig. 5. SESOIL predicts that no leaching occurs beyond 3 m for the first 108 d after application, so the curve is almost totally controlled by the degradation rate. Results from the PRZM, PISTON, and PESTAN models were similar.¹² Monitoring wells at the surface of the saturated zone indicated that 4 to 8% of the applied aldicarb leached below 3 m (see Ref. 12). SESOIL predicted that 7.5% of the applied aldicarb leached below this depth.

Soil samples were collected at 16 different locations at the Lake Hamilton site on five different dates. The mean aldicarb concentrations with depth for these locations are plotted versus the SESOIL predictions for each date in Fig. 6. The predicted concentrations progress away from the soil surface towards the groundwater table slightly faster than the measurements. One possible explanation is that the pollutant cycle of SESOIL does not consider the potential upward movement of the chemical with the upward movement of water due to soil evaporation losses. From the results for Lake Hamilton, it appears that SESOIL does a fair job of predicting the leading edge of the aldicarb profile but tends to be less effective in predicting actual concentration profiles.

Calibrated SESOIL predictions for soil water content at the Fresno, California, site are compared to available measurements (vertically averaged) for the first 3 m of the unsaturated zone in Fig. 7. For this

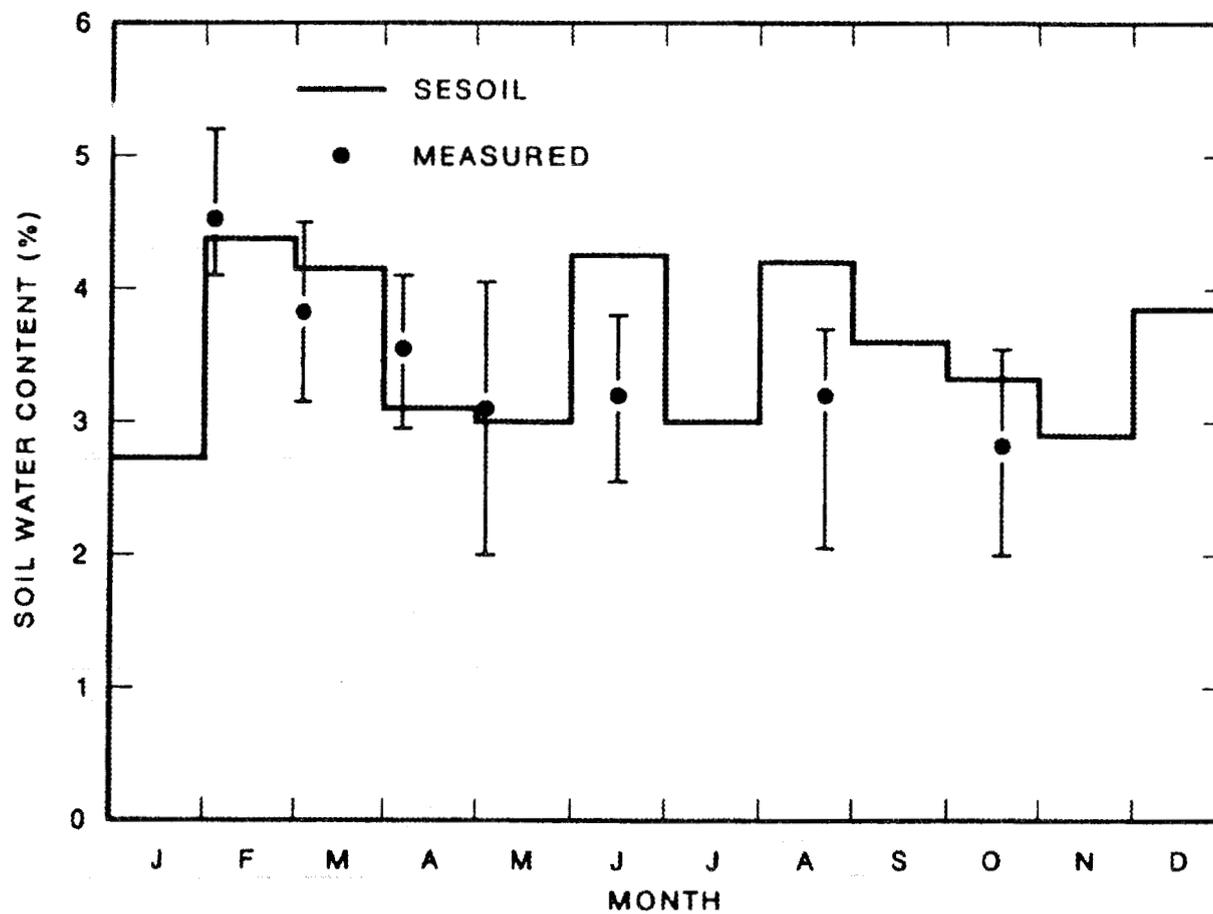


Fig. 3. SESOIL predictions vs measured vertically averaged soil water content for the Lake Hamilton, Florida, site.

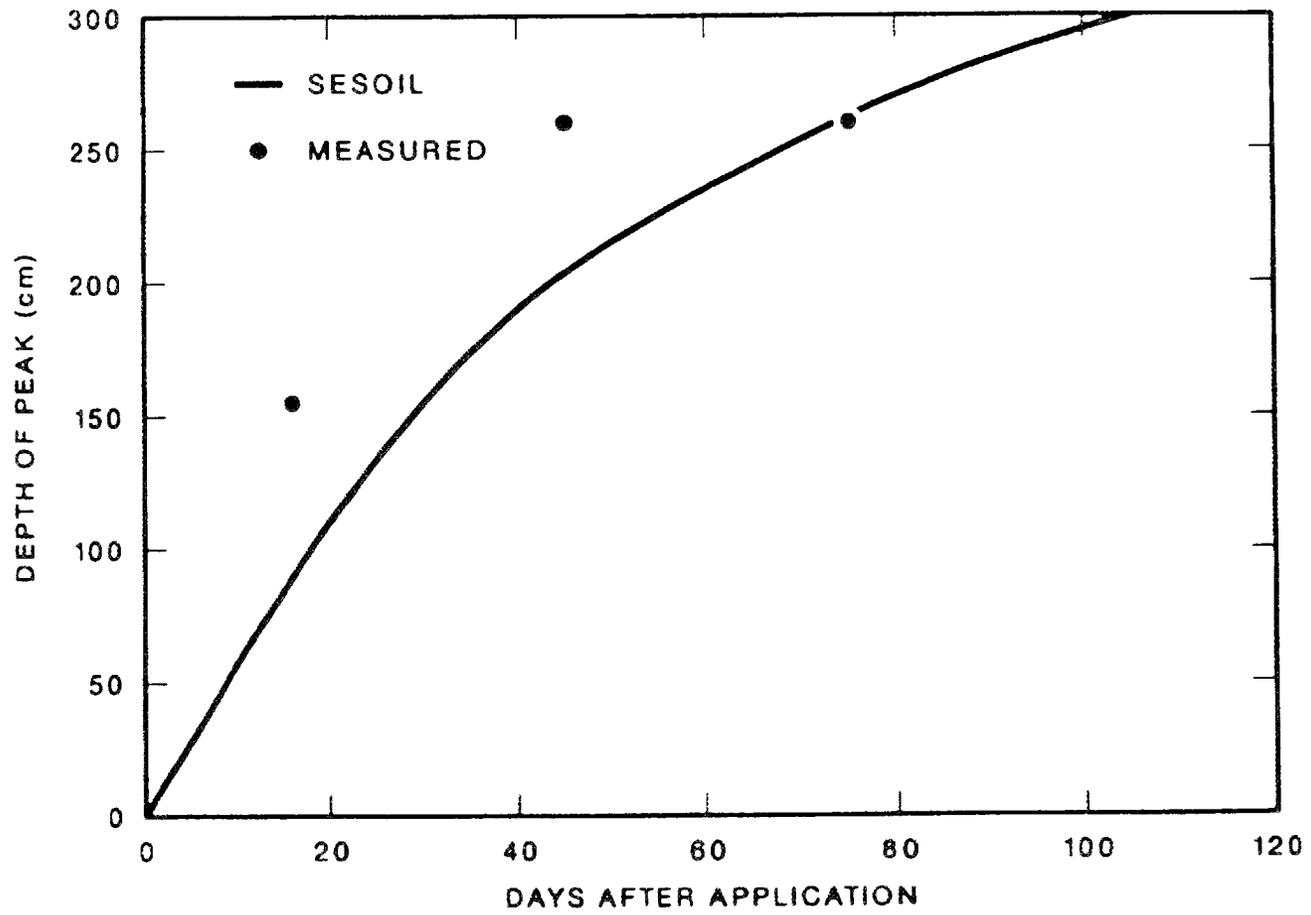


Fig. 4. Predicted movement of aldicarb residues at the Lake Hamilton location.

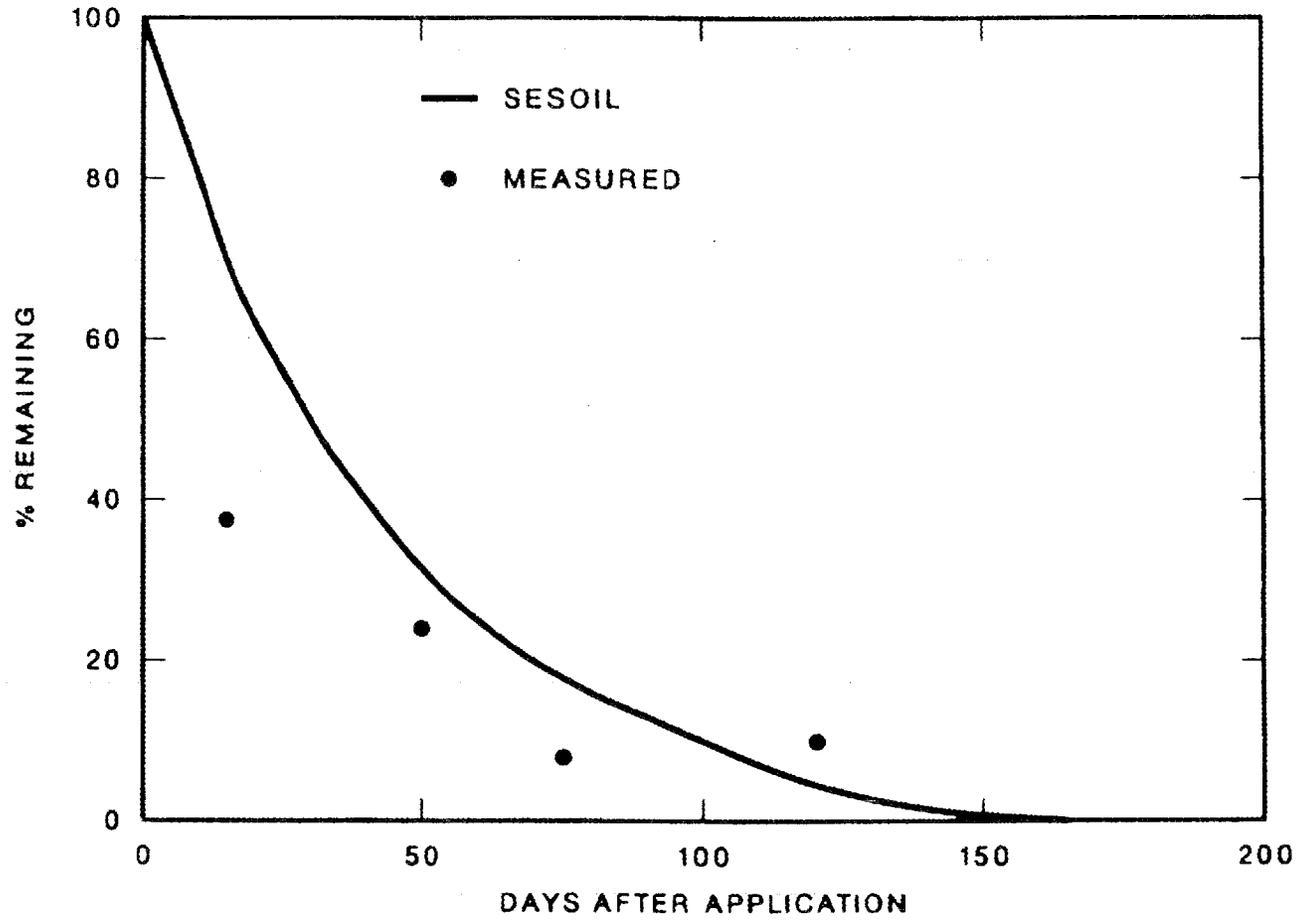


Fig. 5. Predicted amount of aldicarb residues remaining in the upper 3 m of the unsaturated zone at the Lake Hamilton location.

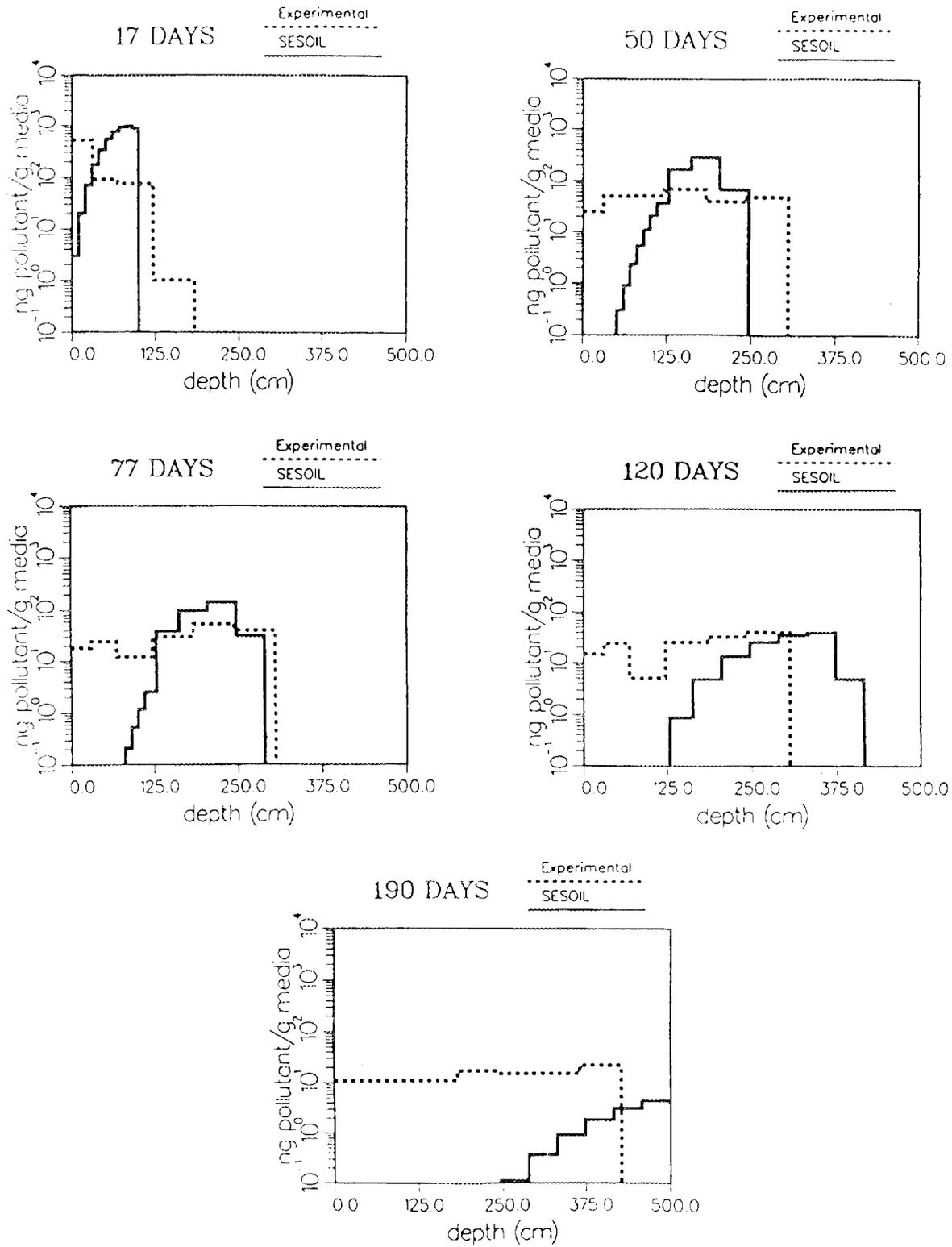


Fig. 6. Results of SESOIL predictions vs measurements at the Lake Hamilton, Florida, site for various days after aldicarb application.

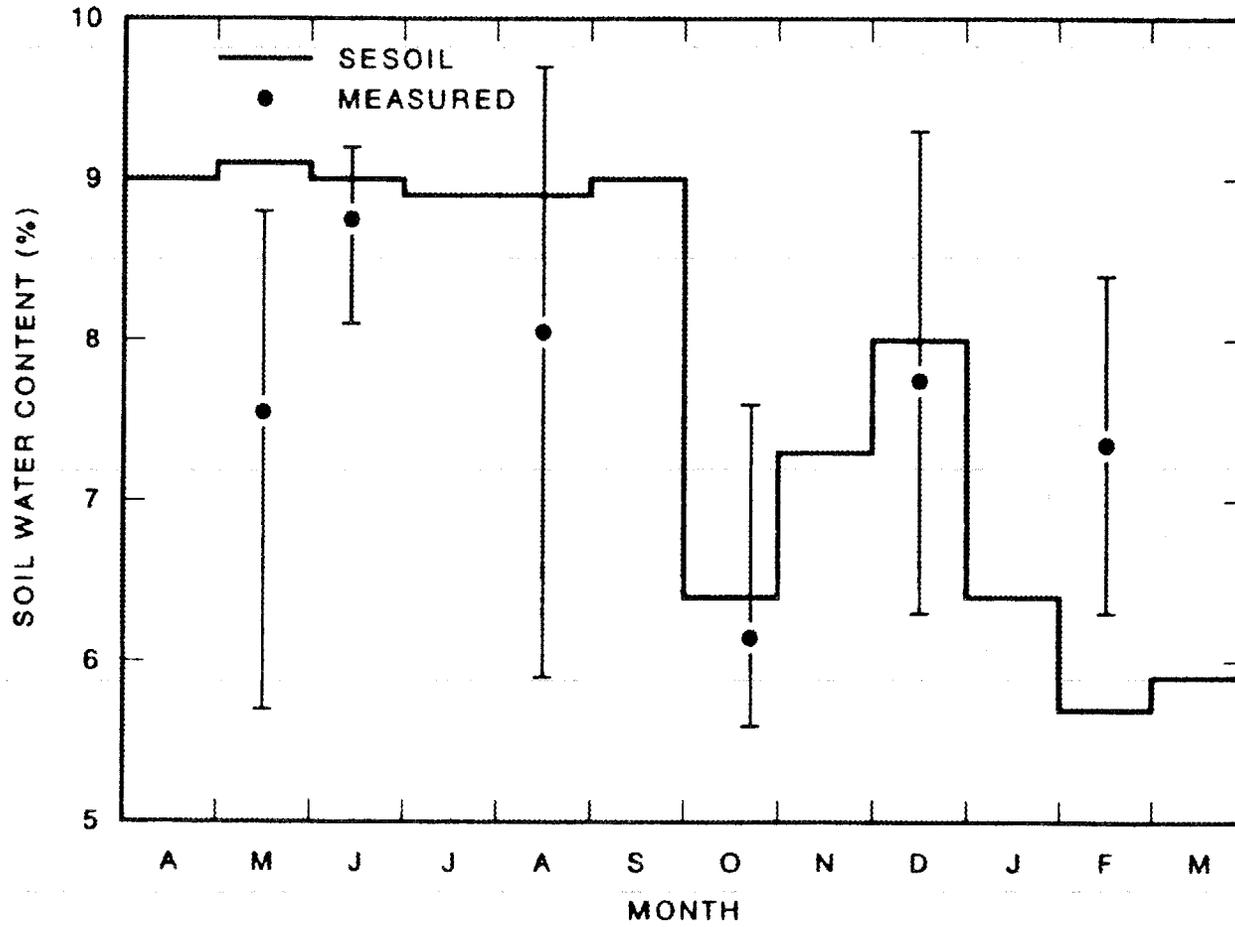


Fig. 7. SESOIL predictions vs measured vertically averaged soil water content for the Fresno, California, site.

site the input values for soil intrinsic permeability K_1 and disconnectedness index c were optimized to obtain the predictions shown. It should be kept in mind that irrigation records were added to monthly rainfall for input to SESOIL. SESOIL predicts a monthly soil water content for the entire soil profile extending from surface to groundwater, whereas the measurements were taken at various depths and only on six dates. Soil water contents would vary significantly depending on when the field plot is flood irrigated. The SESOIL predictions could not be judged given the sparsity of the hydrologic measurements.

Soil samples were taken at 16 different locations at the site on six different dates ranging from 33 to 309 d after the aldicarb treatment. The mean aldicarb concentrations from the 16 cores are graphically displayed vs the SESOIL predictions in Fig. 8. The measured residue concentrations at the first sampling interval (33 d after application) are lower than results from the second sampling date (61 d after application). This probably reflects difficulty in finding the exact location of the two shanks where aldicarb was applied.¹³ Downward movement of the aldicarb residues is quite rapid, which can be attributed to the field being essentially flood irrigated. However, average aldicarb concentrations exceeding 5 ng/g did not occur deeper than 3.0 m. Most of the residues degraded in the upper portion of the unsaturated zone.¹³ The SESOIL predictions for this site show a similarity to those obtained at the Lake Hamilton site. The predicted concentrations progress away from the soil surface faster than the measurements. Again, this is probably due to transpiration tending to retain aldicarb residues in the root zone. Surface evaporation draws soil water and residues from the root zone to the surface.²⁸ SESOIL does not take into account this potential upward movement. Considering that the aldicarb concentrations from the 16 cores were quite variable,¹³ especially in later sampling intervals, SESOIL does a fairly good job of predicting concentration profiles at this site.

The same approach used in the Florida and California field studies to optimize SESOIL predictions to known hydrologic measurements was used for the single-field watershed in Georgia. Measured soil water content and surface runoff were used as calibration endpoints for the hydrologic cycle. Input parameters that were optimized included the intrinsic permeability K_1 , disconnectedness index c , and the mean time of each rainfall event (MTR) for each month.² The information needed for parameter MTR was not available from the data set of Smith et al.¹⁴ Thus, MTR for each month was calibrated to optimize agreement between predictions and measurements for surface runoff. Simultaneously, the values for K_1 and c were adjusted until reasonable agreement was obtained between predicted and observed vertically averaged soil water content. Fig. 9 shows the resultant SESOIL predictions of soil water content versus the measurements (data were unavailable for 1973). Comparisons of observed and predicted monthly surface runoff for 1973 to 1975 are shown in Figs. 10 to 12, respectively. SESOIL predicted a total annual runoff of 24.0 cm for 1973, 14.2 cm for 1974, and 16.5 cm for 1975 (for months January through September); the observed total annual runoff was 23.8 cm for 1973, 12.7 cm for 1974, and 14.0 cm for 1975 (for first nine months). Note that agreement between SESOIL predictions and measurements for surface runoff may not have been as good if actual data were available to derive the parameter MTR. However, in the absence of sufficient data, it

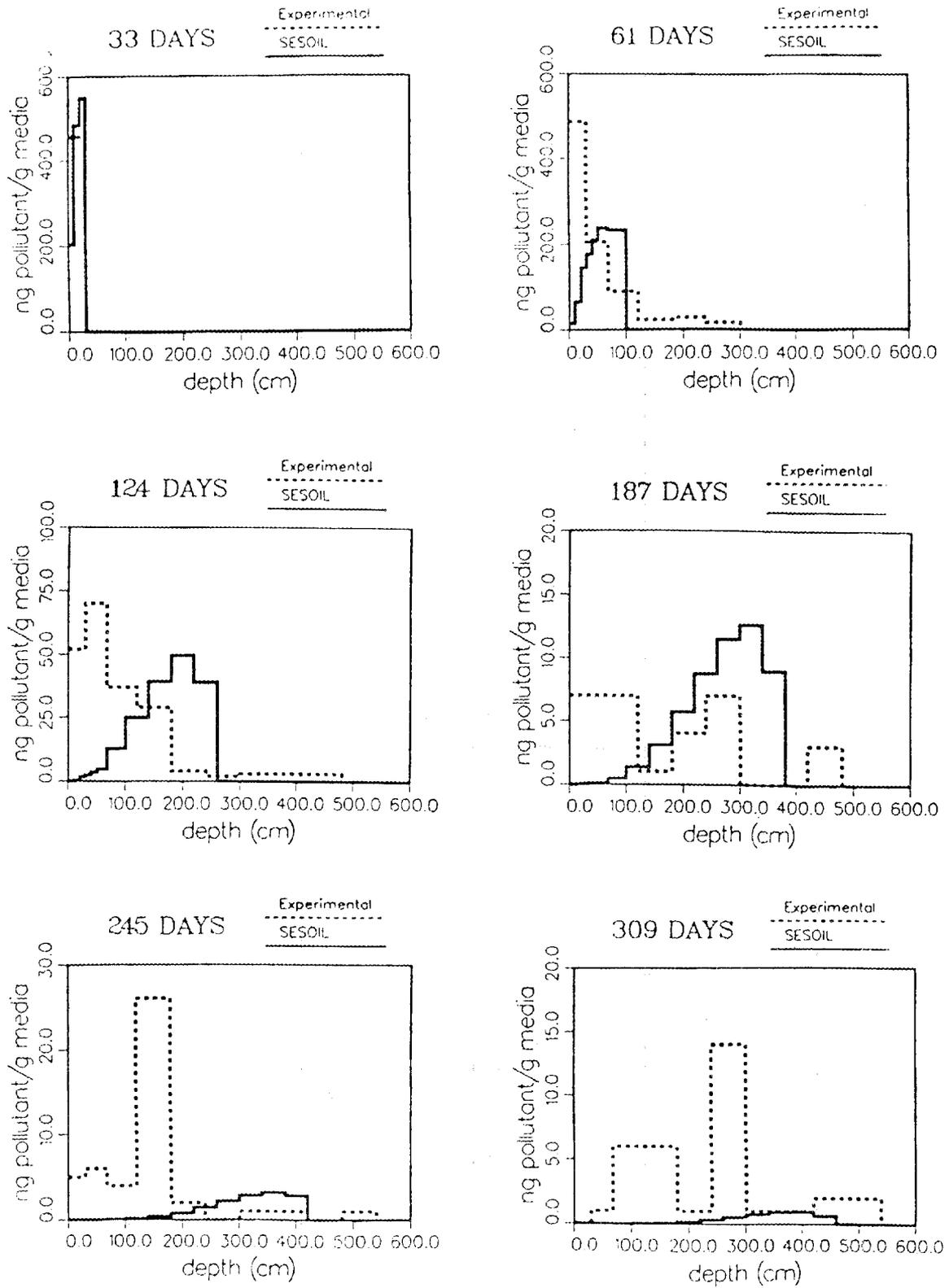


Fig. 8. Results of SESOIL predictions vs measurements at the Fresno, California, site for various days after aldicarb application.

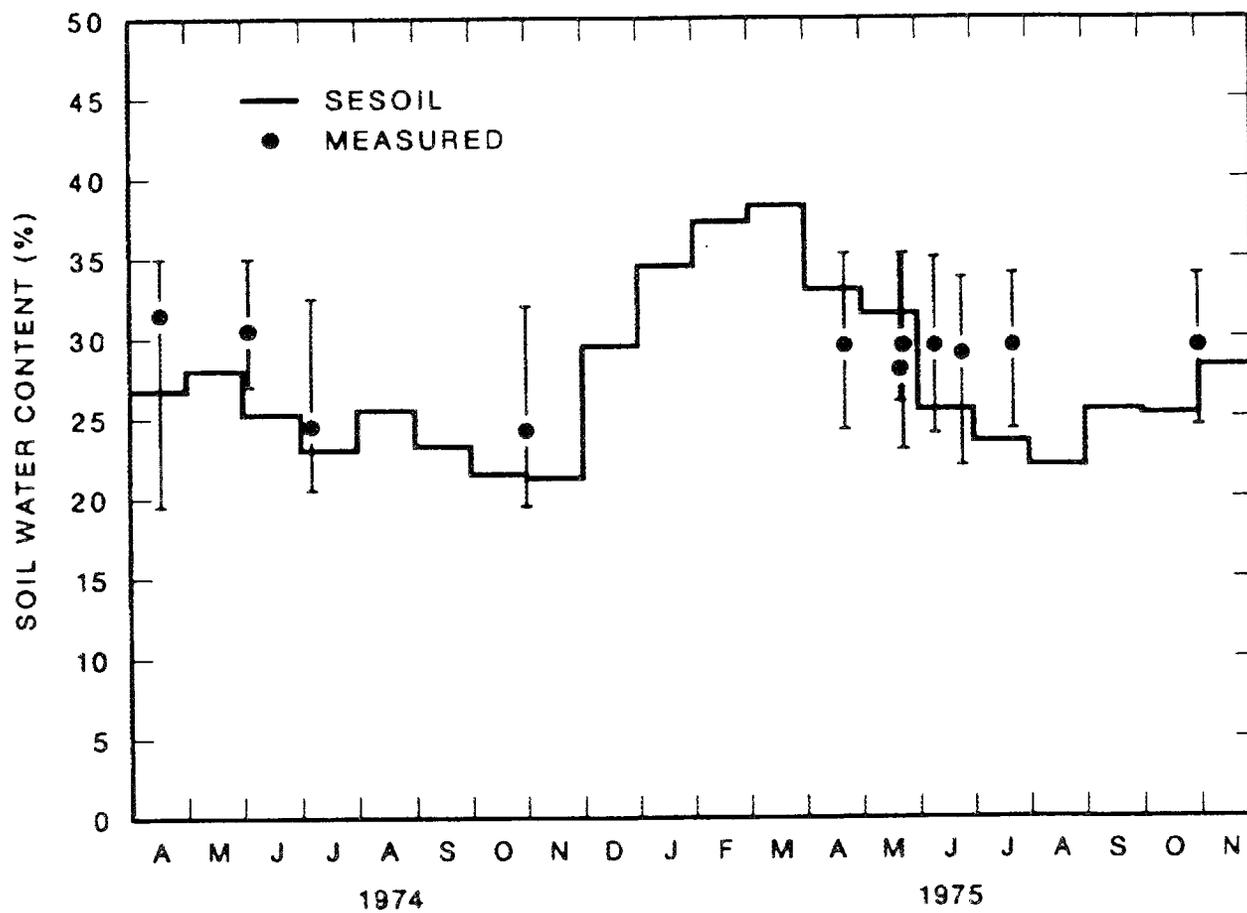


Fig. 9. SESOIL predictions vs measured vertically averaged soil water content for the Watkinsville, Georgia, site.

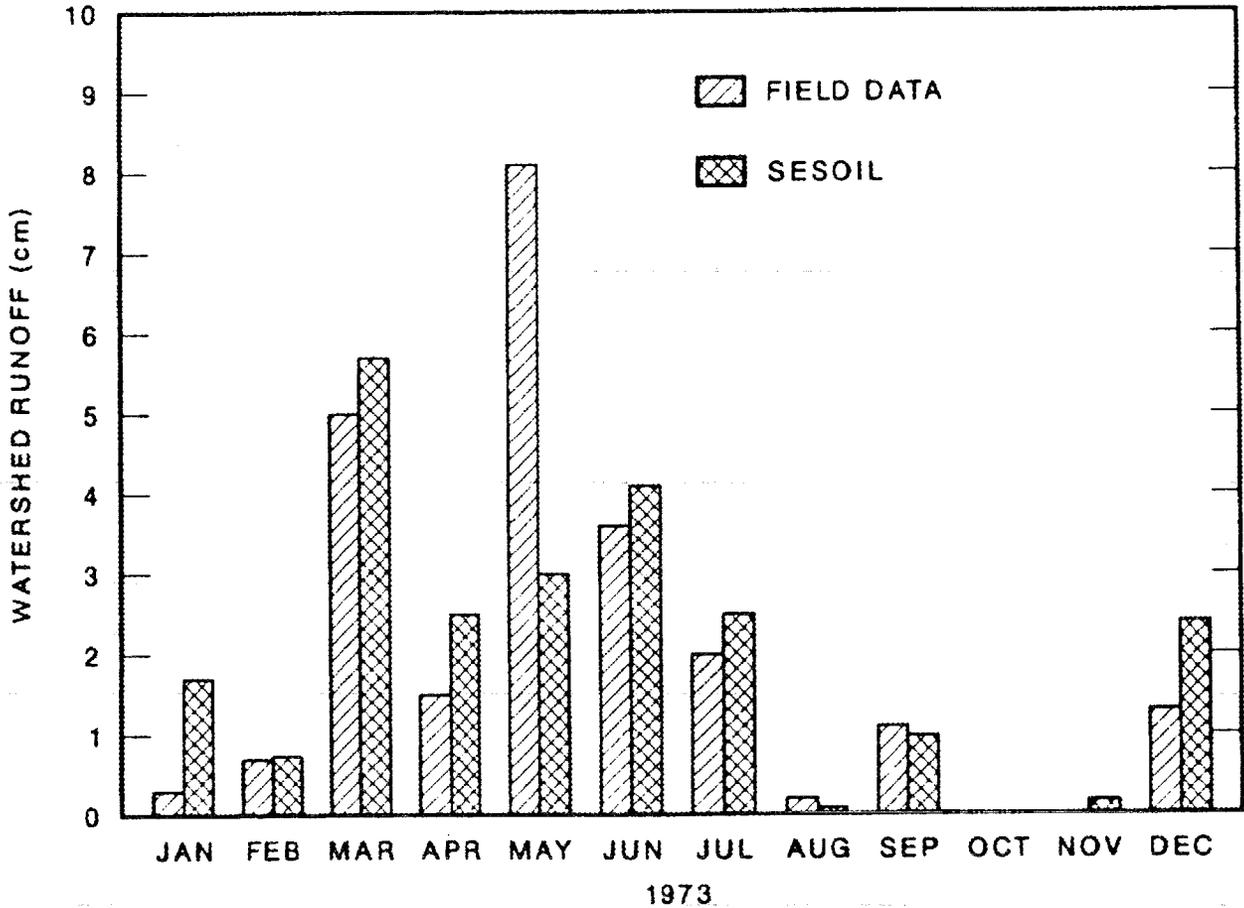


Fig. 10. SESOIL predictions vs observed monthly surface runoff for 1973 at the Watkinsville, Georgia, site.

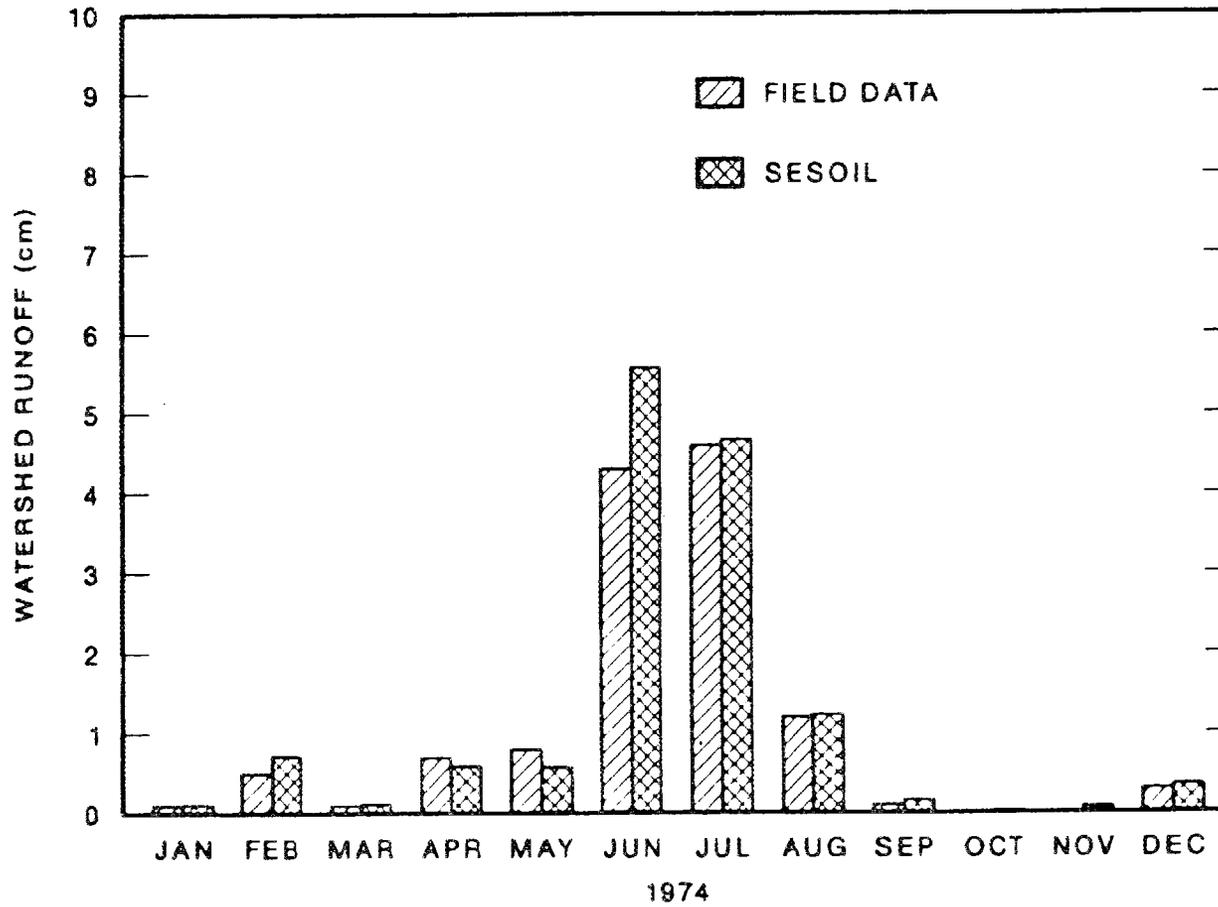


Fig. 11. SESOIL predictions vs observed monthly surface runoff for 1974 at the Watkinsville, Georgia, site.

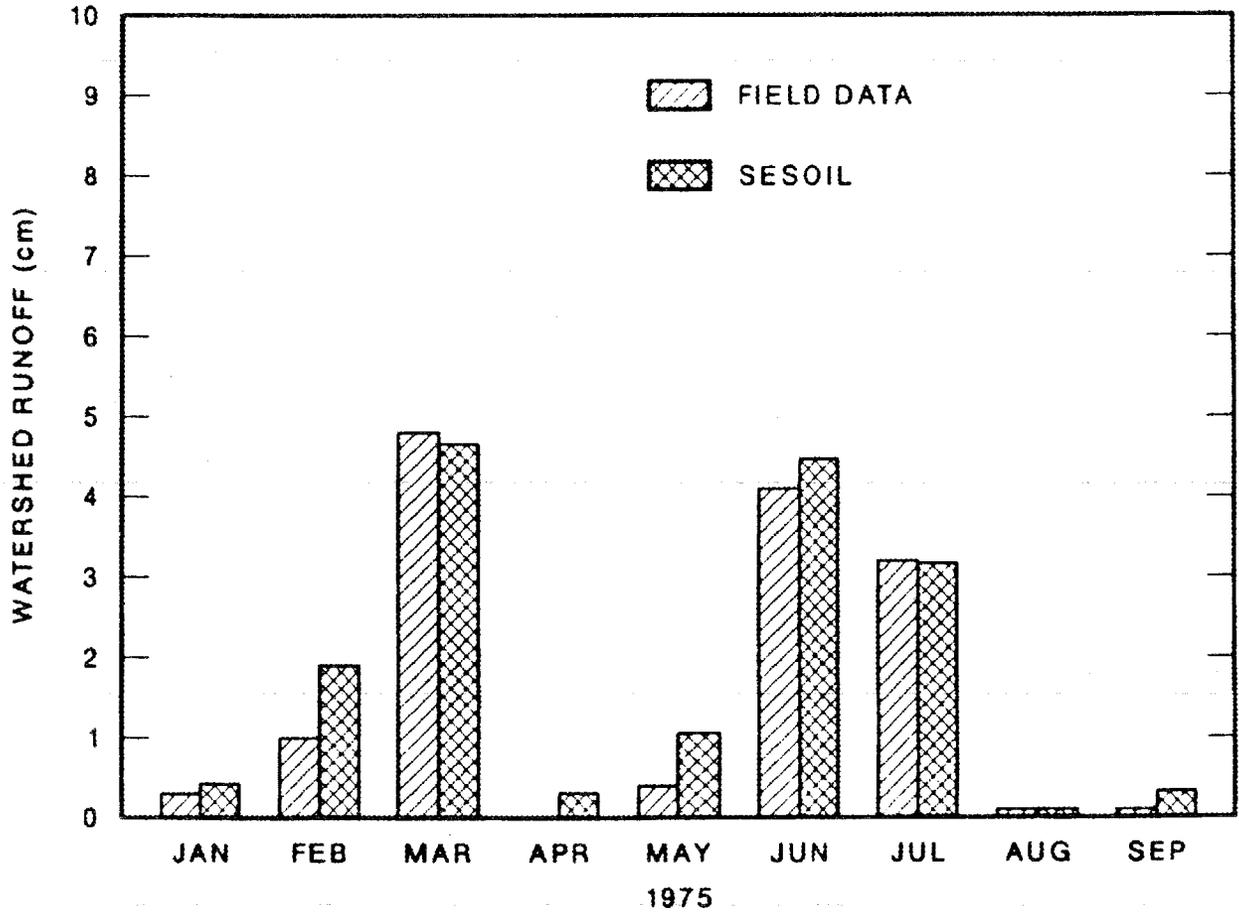


Fig. 12. SESOIL predictions vs observed monthly surface runoff for 1975 at the Watkinsville, Georgia, site.

is always strongly recommended that predictions for the hydrologic cycle be optimized to agree with known measurements.

The atrazine degradation rate and adsorption coefficient were not available from this study and thus initial values used were taken from the laboratory study of Melancon et al.¹⁰ (see Table 1). With these initial values, SESOIL underpredicted the amount of atrazine degraded and predicted that the atrazine peak progressed through the soil profile much faster than the measurements showed. These results showed characteristics very similar to those obtained for atrazine in the laboratory study (see Table 7 and Figs. 1 and 2). Because the model is sensitive to changes for the degradation rate and adsorption coefficient, these two parameters were adjusted until reasonable agreement was achieved with measured concentration profiles for 1973. Another parameter called ISRM,² which controls the amount of chemical partitioned into runoff, was calibrated until the predicted atrazine runoff compared favorably to the measured runoff loss for 1973. Thus, a calibration/validation procedure was used to test the pollutant cycle of SESOIL for this site. The idea was to adjust model parameters until reasonable results were achieved for 1973 and then to validate the model by comparing predictions to measurements for 1974 and 1975. A similar procedure was used by Watson and Brown¹¹ in their testing of the old version of SESOIL. Final calibrated values for the degradation rate and adsorption coefficient were 0.04 d^{-1} and $0.8 \text{ cm}^3 \text{ g}^{-1}$, respectively. These values are well within reasonable limits (e.g., see Dean et al.³²). The calibrated value for ISRM was 0.06, but note that there is no basis for estimating ISRM a priori and it is used here essentially as a fitting parameter.

The final calibrated SESOIL predictions of atrazine concentration profiles are graphically displayed vs the measurements at various times for 1973 in Fig. 13. Note that the measurements vary considerably from May 23 to May 24 due to a rainfall of 1.9 cm on May 23. Predictions for atrazine runoff are compared to measurements in Fig. 14. The total measured atrazine runoff in 1973 was 83.71 g, and the predicted amount was 85.0 g.

With all pollutant-cycle parameters set from calibrating the predictions to measurements for 1973, SESOIL was then used to predict atrazine concentration profiles and runoff for 1974 and 1975. Results for the atrazine runoff are shown in Fig. 14. Annual measured runoff totals were 9.63 g for 1974 and 13.94 g for 1975, while SESOIL predicted totals were 9.38 and 17.18 g for 1974 and 1975, respectively. These results represent a significant improvement over those from the old SESOIL version as reported by Watson and Brown.¹¹ Measured and simulated atrazine concentration profiles are shown in Fig. 15 for various dates in both 1974 and 1975. Once again, it appears that SESOIL does a good job of predicting the leading edge of the chemical profile, but the simulated concentrations at the soil surface underestimate the measurements. Overall, the SESOIL predictions are well within an order of magnitude of the measurements, which is one requirement for screening-level models.

Since predictions for atrazine were in largest disagreement with the laboratory measurements of the chemicals studied (see Table 7), the calibrated values for the degradation rate and adsorption coefficient used for the Georgia watershed were used as input to SESOIL for the laboratory study to check for consistency of results. Significant improvement was

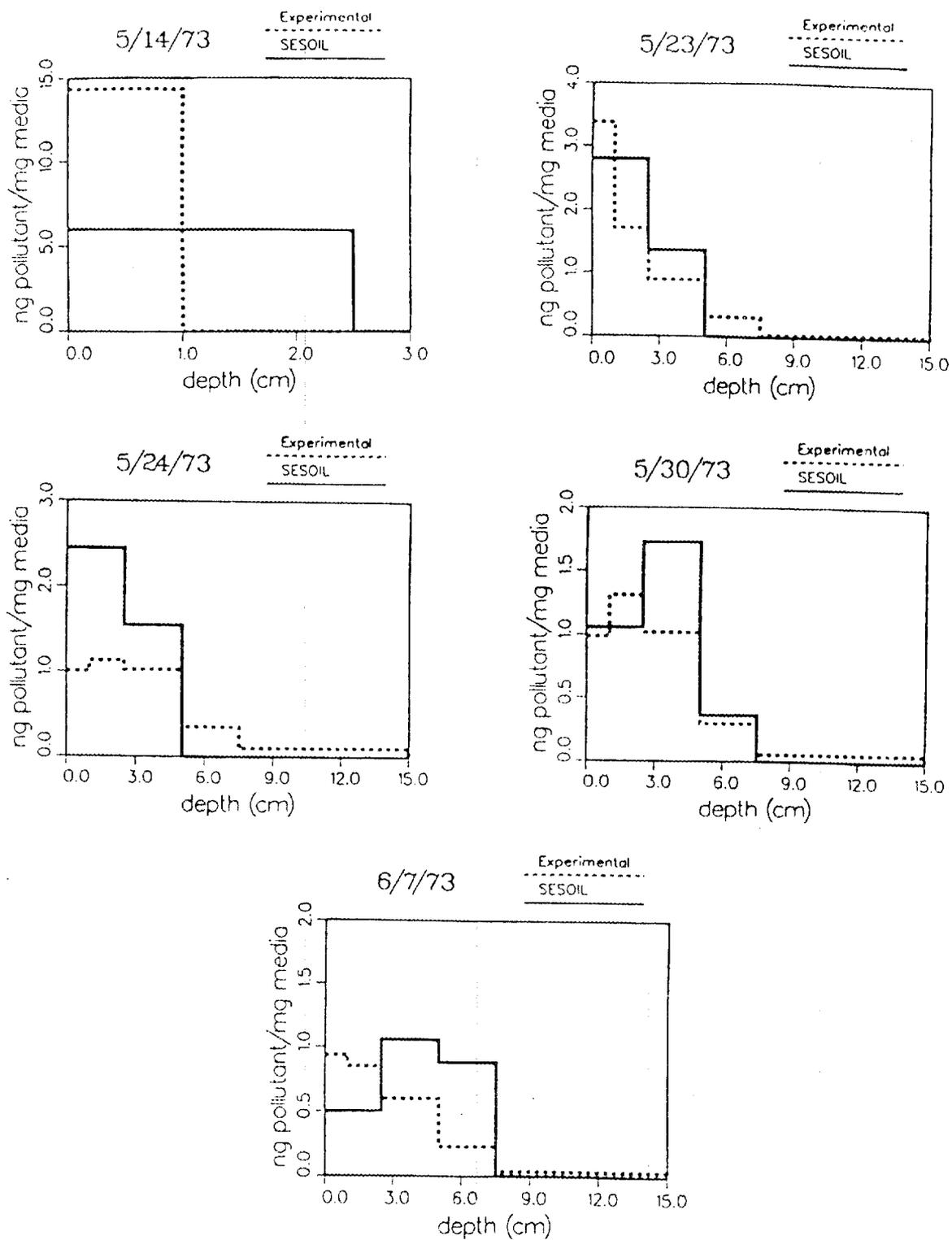


Fig. 13. Results of SESOIL predictions vs measurements at the Watkinsville, Georgia, site for various dates in 1973 after atrazine application.

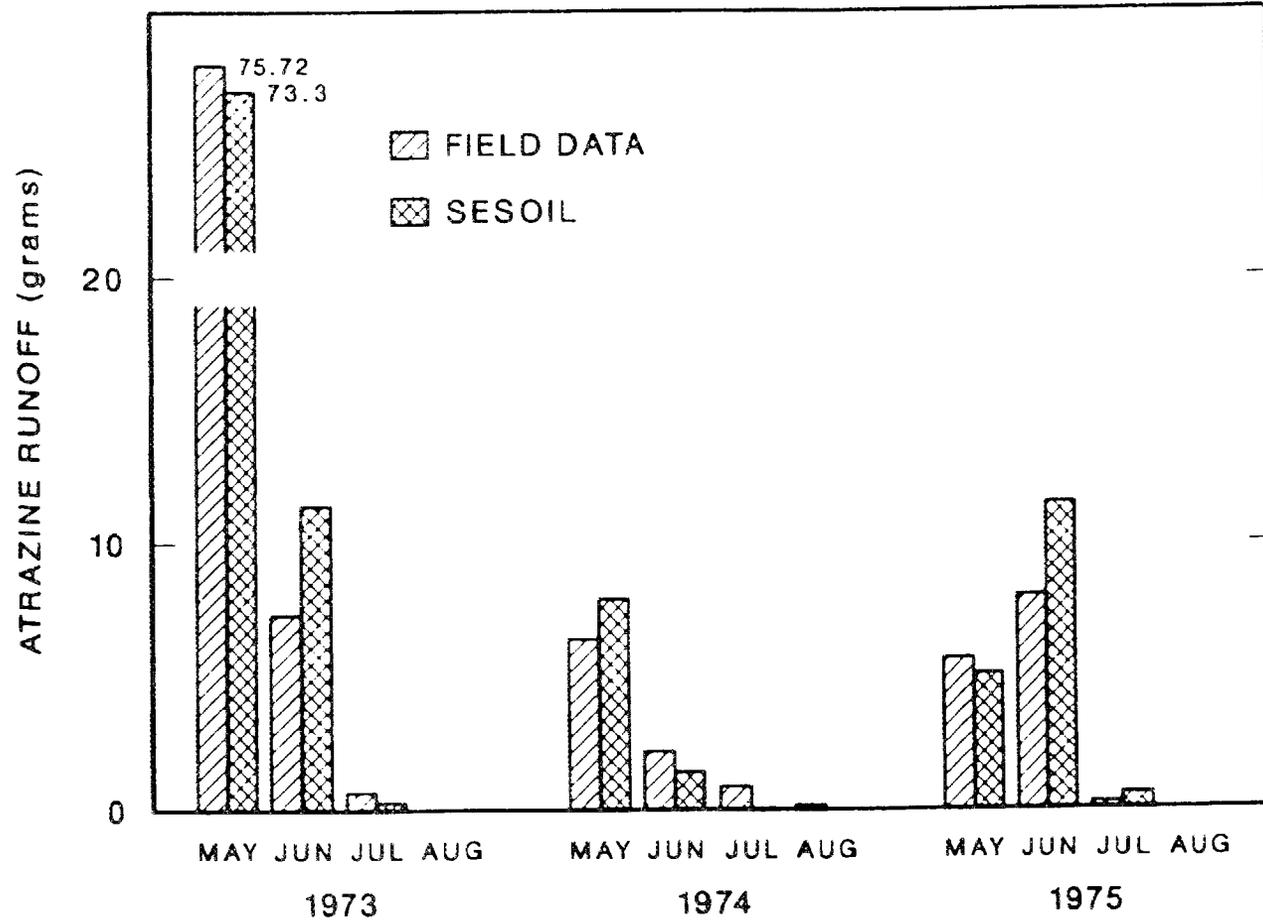


Fig. 14. SESOIL predictions vs observed monthly atrazine runoff for 1973, 1974, and 1975 at the Watkinsville, Georgia, site.

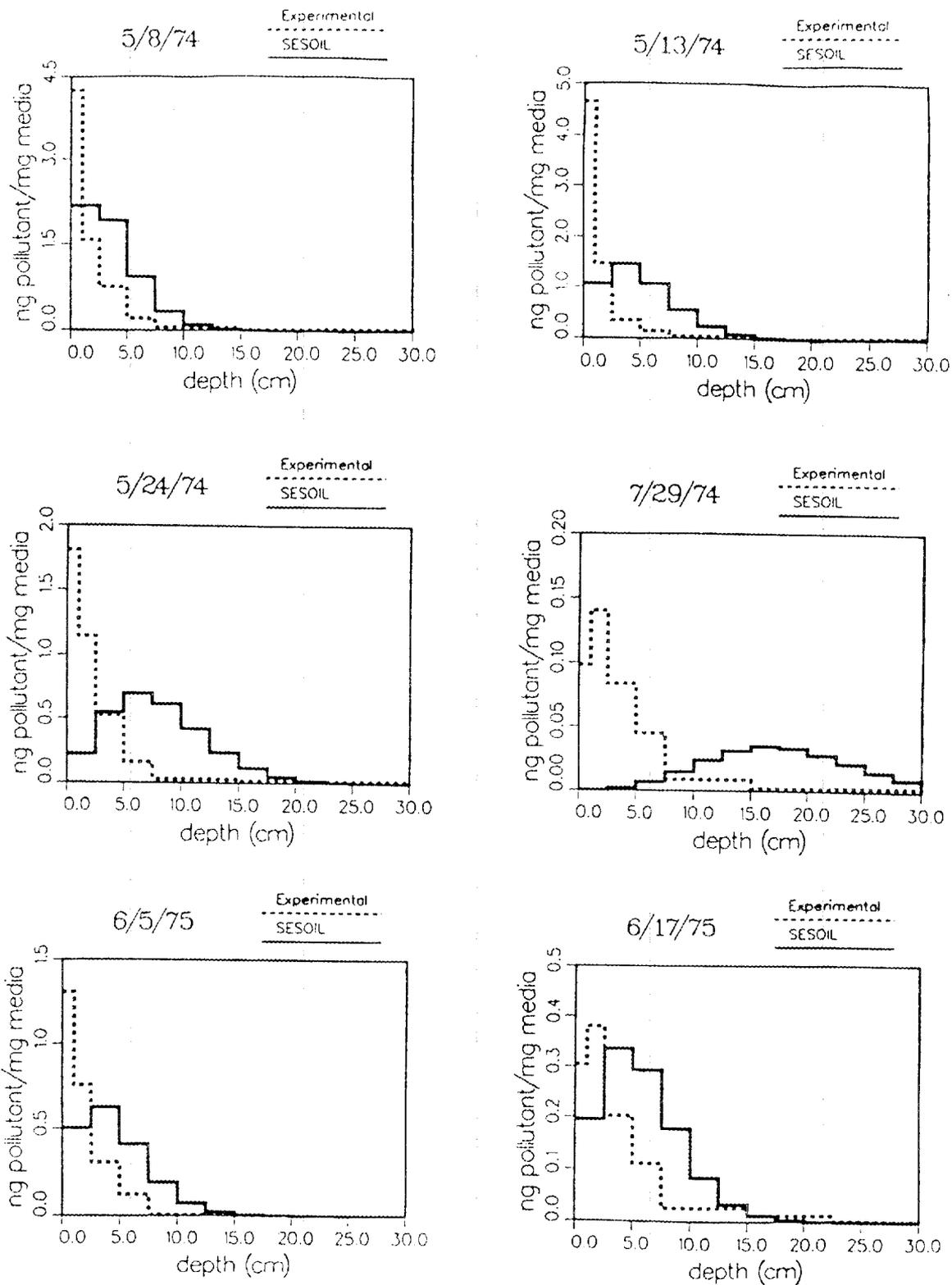


Fig. 15. Results of SESOIL vs measurements at the Watkinsville, Georgia, site for various dates in 1974 and 1975 after atrazine application.

obtained as SESOIL predicted that on day 30 after the atrazine loading, 68.65 mg remained in the soil column, 9.35 mg had leached through the soil column, and 172.5 mg had degraded. These results compare well with the measurements of 94.8 ± 22.2 mg in the soil column, 4.0 ± 2.6 mg in the leachate, and 151.7 mg assumed lost to degradation.

6. CONCLUSIONS

Predictions of the improved version of the screening-level model SESOIL were compared with empirical data from a laboratory study involving six organic chemicals and from three different field studies involving the application of aldicarb to two field plots and atrazine to a single-field watershed. Results for several aspects of pollutant transport were compared including the location of the chemical peak vs time, the time-dependent amount leached to groundwater, the depth distribution of the pollutant at various times, the mass of the chemical degraded, and the amount of pollutant in surface runoff.

Overall, SESOIL model predictions are in good agreement with observed data for both the laboratory study and the field studies. The modified SESOIL does a better job of predicting the leading edge of the chemical profile than the old SESOIL due mainly to an improvement in the pollutant penetration algorithm to include the chemical sorption characteristics. The model is less effective in predicting actual concentration profiles because the simulated concentrations near the soil surface underestimate the measurements. One explanation is that SESOIL does not consider the potential upward movement of the chemical with the upward movement of water due to soil evaporation losses. When a split-sample calibration/validation procedure was used on 3 years of data from the single-field watershed, SESOIL did a good job of predicting the amount of chemical in the runoff.

It is felt that SESOIL can be a useful screening-level chemical migration and fate model. The model is relatively easy to use, input data are straightforward to compile, and most of the model parameters can be obtained or readily estimated. SESOIL can be applied to generic environmental scenarios for purposes of evaluating the general behavior of chemicals. SESOIL should not be applied on a site-specific basis with only limited calibration. Care should be taken when applying SESOIL to sites with large vertical variations in soil properties since the hydrologic cycle of SESOIL assumes a homogeneous soil profile. Thus, it is strongly recommended that predictions for the hydrology at a given site be optimized to agree with known measurements. Caution should be used when making conclusions based on modeling results when little data exist against which to calibrate predictions. However, the simulations in this paper do indicate that SESOIL, when properly used, can be an effective screening-level tool in assessing chemical movement in soils.

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