PESTICIDE TRANSPORT MODELS:

COMPARISON AND VALIDATION WITH SOIL COLUMN LEACHING EXPERIMENTS

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ABSTRACT

Computer models to simulate pesticide transport in the unsaturated zone will be an important management tool in coming years. However, not many efforts were directed to validate the usefulness of such models. In this study, the simulation models GLEAMS, PRZM, and LEACHM were validated. The three models use different mathematical concepts to compute one-dimensional flow and transport in a homogeneous, unsaturated soil. In laboratory experiments, the two pesticides atrazine and terbuthylazine and a conservative tracer were applied to four different soils packed in stainless steel columns. The breakthrough curves obtained from the steady-state unsaturated leaching experiments were compared to the modeling results. The model simulations were based on standard laboratory measurements of the physical and chemical soil-pesticide properties of the sample soils and pesticides. The three models predicted solute breakthrough in general within a factor of two of the measured breakthrough curves. Among the three models, PRZM and LEACHM performed best, while GLEAMS computations are fast at the cost of accuracy.

KEY WORDS: pesticide transport, modeling, validation, GLEAMS, PRZM, LEACHM

INTRODUCTION

In 1983, the European Community introduced new drinking water standards. The new standards allow a maximum total pesticide concentration of 0.5 μg/l including toxic degradation products. The concentration of a single component must not exceed 0.1 μg/l (European Community, 1980). In 1989, Germany adopted these guidelines. Almost 20% of Germany's waterworks cannot comply with the new standards because of elevated pesticide concentrations. Water resources managers, environmental and agricultural agencies as well as farmers are under enormous public pressure to assess the extent and consequences of pesticide contamination in the unsaturated zone between soil surface and ground water table and to contain potential damage to drinking water resources. One of the increasingly accepted tools to support these efforts are computer simulation models.

Over the past twenty years, a number of simulation models were developed to estimate pesticide transport through the unsaturated zone (Donigian 1986). Depending on their application, such models may be classified either as "research models", "screening models", or "management models" a scheme first suggested by Wagenet (1985). "Research models" are intended for scientific studies of transport processes (e.g.: Goltz 1986, Leistra 1979, Selim 1978, Walker 1981). Typically they require extensive, site specific, and often sophisticated data collection. Accurate parameter identification to successfully apply research models is a formidable task. In contrast, quick, comparative analyses for preliminary assessments are obtained from "screening models" (e.g.: Jury 1983, Jury 1984, Stenhuis 1987). Such models describe some important physical features without being applicable to specific field situations. For agricultural and environmental management neither research nor screening models are necessarily very useful.

On one hand, parameter input required for "management models" must be limited to data that are easily measured, readily available from literature and databases, or that can reliably be derived from other available data. On the other hand the use of management models for operation and policy decisions requires rigid concepts that allow realistic estimation of pesticide fate under natural unsaturated conditions. A number of goals are pursued by using models in management. Consequently, a broad range of management models has been developed for a fast growing user community (Banton 1989, Donigian 1986, Melancon 1986).

Despite their popularity, management models still lack a stringent validation with laboratory and field data (Hornsby 1989). Wagenet (1985) emphasized that model validation is crucial to successful applications of computer models. In practice, many models were merely validated with a few sets of field data (Carsel 1986, Jones 1986, Leonard et al. 1988a, 1988b, Smith et al. 1989). Very few attempts have been made to validate and compare pesticide transport models with controlled laboratory soil column experiments (Melancon 1986) or extend these laboratory experiments to controlled field experiments at several distinct measurement and modeling scales.

The goal of this study was to bridge some of the gap between model developers and field researchers, to demonstrate the applicability of computer models under simple 'natural' conditions, and to define a basis for further validation in the laboratory and at existing field sites. Three pesticide transport models were compared and validated with laboratory experiments. This procedure allowed an evaluation of the basic transport and chemistry concepts implemented in these models. Plant related processes (root uptake, transpiration, interception, washoff), surface processes (runoff, erosion, evaporation), and vapor phase transport of pesticides were not included in the evaluation. The field sites from which the soil samples were taken are currently established as research field sites with large lysimeters and a network of monitoring wells and suction lysimeters (Teutsch 1990).

This paper presents the different concepts of the three models, a description of the laboratory experiments and a comparison of model predictions with data obtained from our column studies.

SIMULATION MODELS

The three codes chosen were LEACHM by Cornell University (Wagenet 1989), PRZM by E.P.A. (Carsel et al. 1984), and GLEAMS by the U.S. Department of Agriculture (Leonard 1987). The models represent a variety of different concepts ranging from watershed management applications (GLEAMS) to site specific, research-based applications (LEACHM). Their significant use in environmental and agricultural agencies justifies their common classification as management models.

The basic processes simulated by pesticide fate models are:

- flow of water through the unsaturated zone,
- transport of dissolved contaminants, and
- chemical reactions of contaminants.

The selected models assume one-dimensional flow and transport through a layered, homogeneous soil system. The models distinguish each other primarily by different combinations of concepts to simulate flow and transport. Plant uptake of water and pesticides, evapotranspiration, vapor transport, overland flow, and erosion are also simulated in all or some of the three models. The latter processes will not be investigated in this study.

Chemical Processes Simulation

The chemical processes considered in the three models are sorption and degradation of pesticides. The assumptions regarding these processes are the same for all three programs. Sorption processes are simulated with a linear sorption isotherm assuming instantaneous, reversible adsorption:

$$c_s = K_d * c_l \qquad (1)$$

c_s: concentration of adsorbed solute [mg/kg]
c_l: concentration of dissolved solute [mg/l]
K_d: sorption partition coefficient [l/kg]

$$\frac{dc}{dt} = -k * c \qquad (2)$$

c: total solute concentration [mg/l]
t: time [days]
k: degradation constant [1/days]

A simple approach to estimate chemical and microbial degradation is the use of a first-order decay equation:

The degradation rate constant k is directly related to the theoretical half-life of a pesticide:

$$t_{1/2} = \frac{\ln 2}{k} \qquad (3)$$

Both the rate constant k and the partition coefficient K_d are soil-type and pesticide specific. The partition coefficient often appears in a form that is normalized with respect to the organic carbon content OC:

$$K_{oc} = \frac{K_d * 100}{\%OC} \qquad (4)$$

K_{oc} is used as a soil-independent parameter, even though the dependence of K_d on OC is usually limited (Rao 1980, Goring 1972). Further discussion of these equations are found in a number of excellent reviews concerning pesticide sorption and degradation processes (Guenzi 1974, Hern 1986, Jury et al. 1987, Khan 1980, Neely 1985).

GLEAMS: Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) was introduced by Leonard (1987) as PC version of the agricultural watershed model CREAMS (Knisel 1980). The new version included a pesticide transport model for the root zone. Of all three models GLEAMS is the only one intended to simulate not only pesticide fate within the soil but also within other subsystems of a small watershed (overland flow, channel flow). Being a general model, the concepts of the different system components are based on simple mathematical approximations.

Daily infiltration rates are calculated based on the amount of rainfall using the Soil Conservation Service curve number equation (USDA 1972). Water flow through the root zone is simulated by a cascade model ('tipping bucket' model) in which the soil column is represented by seven computational layers. The cascade model consists of a simple adding and subtracting algorithm based on each layer's actual water content, total porosity, and field capacity. Transport of pesticides is calculated in a similar fashion: At each time-step (each day), GLEAMS initializes the transport routine by calculating first-order decay of the total (dissolved plus adsorbed) pesticide concentration:

$$c_{i_{end}} = c_{i_{beg}} \exp(k*1) \qquad (5)$$

c: total solute concentration[mg/l]
i_{end}: layer i at the end of the day
i_{beg}: layer i at the beginning of the day

The concentration of pesticide in solution becomes:

$$c_{l_i} = \frac{c_{i_{end}}}{K_{d_i}*\rho_i + \theta_i} \qquad (6)$$

ρ: bulk density [kg/l]
θ: soil moisture content []

The total mass m of pesticide percolating into and out of layer i is determined from:

$$m_{inc_i} = c_{l_{i-1}} * Q_{inc_i} \qquad (7)$$

$$m_{out_i} = c_{l_i} * Q_{out_i}$$

Q_{inc}: inflow

Q_{out}: outflow

At the end of each time-step the mass of pesticide inflow and outflow are added and subtracted, respectively, to and from the total pesticide mass of layer i before the redistribution.

PRZM: The Pesticide Root Zone Model (PRZM) (Carsel et al. 1984) was developed at E.P.A. to support their decision making process. PRZM is a strictly one-dimensional model to predict the fate of pesticides in the unsaturated zone. PRZM uses a modified version of the SCS curve number technique to distribute the amount of rainfall into an infiltration and a runoff component. As in GLEAMS, the application of the SCS curve number technique limits the smallest computational time-step to one day. Water flow within the root zone is determined by a 'tipping bucket' model similar to the one used by GLEAMS. However, the model soil column can be divided into several dozen computational layers (GLEAMS: seven) defined by the user. In contrast to GLEAMS, PRZM applies the well-known 1-D advection-dispersion equation to calculate pesticide transport. The advection-dispersion equation includes terms to consider linear adsorption and first-order degradation:

$$\frac{\delta(c_l*(\theta + K_d*\rho))}{\delta t} = D*\frac{\delta^2(c_l*\theta)}{\delta x^2} - \frac{\delta(c_l*\theta q)}{\delta x} - \lambda*c_l*(\theta + K_d*\rho) \qquad (8)$$

The differential equation is solved with an implicit finite difference scheme. The flow-rate q is determined at each time-step from the flow computation. In PRZM, the hydrodynamic dispersion coefficient D [cm^2/d] is a velocity-independent input variable. D is a factor to describe the effects of diffusion and travel path tortuosity. The upper boundary condition is a prescribed concentration (Dirichlet-type). At the lower boundary a unit gradient condition (Neumann-type) is used.

LEACHM: Of the three models chosen, the Leaching Estimation And CHemistry Model (LEACHM) (Wagenet 1987) is certainly the most sophisticated model - conceptually as well as numerically. Instead of the 'tipping bucket' approach LEACHM applies the unsaturated flow equation, commonly known as Richard's equation, to simulate water flow through the unsaturated zone:

$$\frac{\delta\theta}{\delta t} = \frac{\delta K_u(\theta)}{\delta z} + \frac{\delta}{\delta z}(D(\theta) * \frac{\delta\theta}{\delta z}) \qquad (9)$$

with:

$$D(\theta) = \frac{K_u(\theta)}{C(\theta)} \qquad C(\theta) = \frac{\delta\theta}{\delta\psi}$$

θ: water content []
ψ: water suction potential [L]
$K_u(\theta)$: unsaturated hydraulic conductivity [L/T]
$D(\theta)$: hydraulic diffusivity [L^2/T]
$C(\theta)$: specific water capacity [1/L]
z: elevation [L]

The application of this equation requires two additional functions to describe $K_u(\Theta)$ (unsaturated hydraulic conductivity function) and $\varphi(\Theta)$ (water retention function). For LEACHM, a modified version of Campbell's two-parametric unsaturated conductivity and water retention equation was developed (Hutson 1987):

$$\psi = a * \frac{(1 - \frac{\theta}{\theta_s})^{\frac{1}{2}} * (\frac{\theta_c}{\theta_s})^{-b}}{1 - (\frac{\theta_c}{\theta_s})^{\frac{1}{2}}} \quad \text{for } \psi_c > \psi > 0 \qquad (10)$$

$$\psi = a * (\frac{\theta}{\theta_s})^{-b} \quad \text{for } \psi > \psi_c$$

with:

$$\psi_c = -\frac{2b * \theta_s}{1 + 2b}$$

θ_s: water content at saturation
θ_c: water content at air-entry

The two empirical parameters a and b are obtained by fitting the theoretical function (10) to experimental water retention curves. This is an important conceptual difference to GLEAMS and PRZM, where water content at the wilting point, field capacity, porosity and a drainage factor/saturated hydraulic conductivity are the parameters required to simulate water flow.

Equation (9) is solved numerically using a finite difference technique. Boundary conditions must be defined by the user depending on the conditions to be modeled. Discretization of the finite difference domain is also user-dependent. The time-step in LEACHM varies with the change of flow rates and may be very short (parts of seconds).

Similar to PRZM, LEACHM applies the 1-D advection-dispersion equation (8) for transport simulation. The equation is solved simultaneously with Richard's equation by also using a finite difference technique. In contrast to PRZM, however, the hydrodynamic dispersion coefficient D is not independent from velocity and water content: At each time-step, D is determined as the sum of the unsaturated diffusion coefficient $D_m(\theta)$ and the dispersion coefficient $D_s(v)$ with:

$$D_m(\theta) = D_0 * a * \exp(b * \theta) \qquad (11)$$

$$D_s(q) = \alpha * \frac{q}{\theta}$$

D_0: diffusion coefficient for water $[L^2/T]$
a, b: empirical constants
α: dispersivity [L]

D_m was negligible during our laboratory studies. The dispersivity α is a soil specific parameter.

MATERIALS AND METHODS

Soils and Pesticides

Soil samples were taken from two agricultural sites. At the Horkheim site (near Stuttgart) the soil is a fine sandy, silty loam with moderate to high organic carbon content. The Ahlum site (near Braunschweig) consists of a thick loess soil with low to moderate organic carbon content. 100 separate samples were taken from the upper two soil horizons at each site (total of 400 samples combined to four volume samples). The sampling grid was a regular net of 5 by 20 points on 10 m by 47.5 m (Horkheim) and 7 by 14 points on 12 m by 25 m (Ahlum). The samples were sieved, mixed, air-dried, and stored at 5°C. For simplicity, the four soil samples were named Hk03 (A-horizon Horkheim), Hk36 (top B-horizon Horkheim), Ah03 (A-horizon Ahlum), and Ah36 (top B-horizon Ahlum).

Atrazine and terbuthylazine were used as pesticides. Bromide was applied as a conservative reference tracer in separate, identical column experiments. The two pesticides are commonly found in weed control, particularly for corn crops. Atrazine has been detected in many drinking water wells across Germany. After the government restricted the use of atrazine, terbuthylazine replaced atrazine in most areas.

Unsaturated Leaching Experiments

The unsaturated soil column leaching experiments were conducted in stainless steel columns of 30 cm length and 10 cm diameter (Fig. 1). The four columns were packed (from bottom to top) with 1 cm gravel (grain size 2-4 mm), 20 to 25 cm air-dried, homogenized soil, and 1 cm medium sand. The column filling was contained by two stainless steel sieves at the top and the bottom of the filling. The column bottom was funnel-shaped to collect percolate. Over a three month period, 14.9 mm de-ionized water was applied daily by a column irrigation apparatus placed on top of the column. The total daily amount of precipitation was applied within a two-hour period. Daily samples of percolate were collected immediately before the beginning of the next irrigation cycle. The measurement scale (1 day) led to the observation of a (pseudo-) steady state unsaturated flow. Both pesticides were applied simultaneously (500 g/ha) at the 10th day of the experiment. At that time the columns had reached a constant water content ("field capacity"). Bromide leaching experiments were conducted under the same conditions. Percolate was analyzed for pesticide and bromide concentrations, respectively.

Model Input Parameter Measurements

All input parameters necessary to run the three pesticide transport models were measured employing standard laboratory procedures for the four soil samples and for both pesticides. Table 1 provides a list of the parameters measured.

Soil texture was determined with standard sieving and sedimentation methods. Bulk density, total porosity and field capacity were obtained directly from the columns of the leaching experiments. Field capacity was defined by the average water content of the unsaturated soil columns 22 hours after each irrigation. Water retention curves of the four soils were determined at eight pressure head points between 0 and -1500 kPa. The parameters a and b of the modified Campbell equation (10) were determined by graphically fitting the theoretical curve to the experimental results.

Hydraulic conductivity and dispersivity were measured under saturated conditions in soil columns identical to the columns used for the pesticide leaching experiments. Dispersivity was determined by fitting experimental breakthrough curves of chloride to the advection-dispersion equation for saturated transport. Unsaturated dispersivities were obtained from the breakthrough curves of the bromide leaching experiments. For practical purposes, dispersivity is measured much faster with saturated tracer experiments than with unsaturated experiments (Harter 1989).

Organic carbon content was determined by the Lichterfeld-method (DIN 19684). To determine the adsorption distribution coefficient a saturated sample of each soil was equilibrated with a known amount of each pesticide at $4^{\circ}C$ for 24 hours. The samples were then shaken for an hour, filtered, centrifuged and analyzed for pesticide concentration in the filtrate. It should be noted that a number of procedures exist to determine the distribution coefficient. The results of various methods, however, may be different.

Degradation experiments were implemented to determine the half-life of the pesticides in each soil sample. For both pesticides 10 to 13 probes of each of the four soil samples were prepared with a solution containing 1 µg/l pesticide. The samples were stored at 80% water holding capacity and 20°C. Subsequently, one sample per week was removed from storage and analyzed for residual concentration. The degradation coefficients were determined from regression analyses.

All pesticide analyses were performed using gas-chromatography after filtration and extraction. Bromide samples were analyzed using ion-chromatography.

Fig. 1: Schematic diagram of soil columns for pesticide leaching experiment.

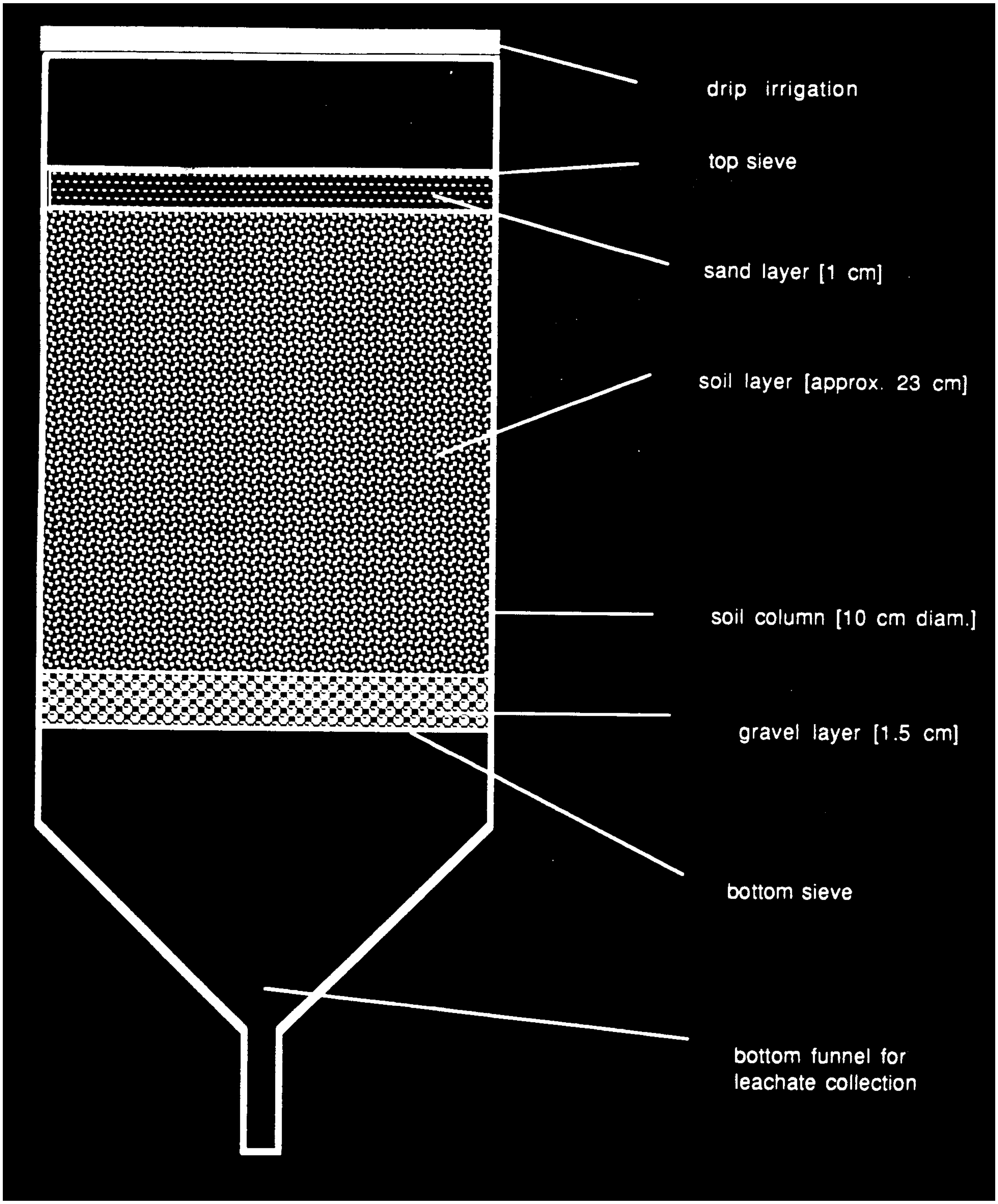

drip irrigation
top sieve
sand layer [1 cm]
soil layer [approx. 23 cm]
soil column [10 cm diam.]
gravel layer [1.5 cm]
bottom sieve
bottom funnel for
leachate collection

Table 1: Soil-pesticide physical and chemical parameters measured in laboratory analyses for data input and methods of analyses.

soil parameters:	soil texture	sieve- and sedimentation-analysis
	water content	gravimetric
	specific soil density	volumetric
	bulk soil density	gravimetric
	total porosity	gravimetric
	effective porosity	column tracer study
	field capacity	gravimetric
	water retention curve	hanging water column, pressure cell
	saturated hydraulic conductivity	permeameter
	saturated dispersivity	column tracer study
	organic carbon content	Lichterfeld-method, DIN 19684
pesticide parameters:	distribution coefficient	batch equilibrium
	degradation half-life	batch degradation study

Computer Simulations

The simulations with GLEAMS, PRZM, and LEACHM were run on an IBM compatible PC-AT. The programs were written in FORTRAN. We used GLEAMS version 1.8.54 (released in May 1989), PRZM release 1 (December 1984), and LEACHM version 2 (June 1989). Two approaches were taken to compare the models and validate the results: First, the models simulated the breakthrough curves of the unsaturated leaching studies with atrazine, terbuthylazine, and bromide using the soil-pesticide parameters determined in standard laboratory analyses as described above. Second, the results of the computer simulations were fitted to the measured breakthrough-curves of the leaching experiments by optimizing the distribution coefficient K_d, degradation half-life $t_{1/2}$, and dispersivity α. Sensitivity analyses showed that these parameters had most impact on model results. Four quantities were compared to the experimental breakthrough curves (BTCs) to interpret the results of the model simulations: BTC arrival time, BTC peak arrival time, BTC peak concentration, and total mass of solutes.

RESULTS AND DISCUSSION

Parameter Analysis

A summary of the soil-pesticide parameters determined in the laboratory is given in table 2. Average saturated dispersivity values of the four soil samples varied between 0.16 and 1.5 cm with coefficients of variance of 10% (Hk36), 21% (Ah36), 38% (Ah03), and 80% (Hk03). In contrast, dispersivity values obtained from the unsaturated bromide leaching experiments were all below 0.2 cm. These results show that dispersivity values from saturated experiments give only a rough estimate of unsaturated dispersivity.

Distribution coefficients K_d varied from 0.6 to 1.1 [l/kg] for atrazine, and from 0.7 to 5.8 [l/kg] for terbuthylazine. K_{oc} values along the two horizons corresponded well at each single site. However, K_{oc} values of the two sites were significantly different from each other showing that K_{oc} values of a pesticide are not applicable to any soil.

Theoretical first-order degradation curves closely followed experimental data. Regression analyses yielded correlations (r^2) of 84% to 99% with the exception of Hk36 (atrazine: 77%, terbuthylazine: 61%). Half life values ranged from 69 days to 250 days for terbuthylazine and from 44 days to 143 days for atrazine.

Model Prediction without Calibration

The values shown in table 2 were used as input parameters for the model simulations with GLEAMS, PRZM, and LEACHM. Model computation times varied significantly. GLEAMS simulated transport of 10 pesticides in a single run, while PRZM only simulated one pesticide case at a time. Both codes implemented approximately two to three runs per minute. In contrast, a single LEACHM run needed approximately one hour of computation time for the simultaneous computation of four pesticides. The additional computation time in LEACHM stemmed from its transient water flow calculations at a scale that is several orders of magnitudes finer than one day. Coarser time-scale discretization and introducing equivalent steady-state rainfall input would significantly reduce computation time with LEACHM at the cost of model accuracy.

All three models accurately predicted the (pseudo) steady-state flow through the columns. Bromide simulations (fig. 2), however, revealed significant differences between the transport predictions of the three models that clearly reflected the models' complexity. Pesticide fate and transport predictions followed similar patterns (fig. 3-4), although not as pronounced as in the case of bromide.

GLEAMS simulations were characterized by breakthrough curves that yielded extremely conservative estimates. In all cases, GLEAMS overestimated peak travel velocity (by up to a factor of four) and total mass of leachate (by up to a factor of 3). Calculated peak concentrations deviated by a factor of 2 from measured values. Fast BTC peaks were underestimated, slow BTC peaks overestimated. Most strikingly, all simulated BTCs began at the day of solute application even if pesticides were strongly adsorbed (e.g. terbuthylazine in Hk03). Realistic estimates of the BTC arrival times were not possible. While the measured BTCs showed a wide variety of shapes over a large range of peak concentrations, GLEAMS simulations were rather similar for the four different soils, particularly in the case of atrazine. The modeling results suggest that the use of GLEAMS for comparative studies of pesticide transport would significantly underestimate the true span of soil-pesticide interactions and hence of consequences on groundwater pollution.

Table 2. Average values of all measured parameters used for model data input.

	Hk03	Hk36	Ah03	Ah36
pesticide leaching soil columns:				
length of soil column [cm]	23.3	23.7	23.4	23.4
bulk density [g/cm^2]	1.25	1.22	1.15	1.21
total porosity [%]	53	55	56	53
field capacity [%]	47.4	44.9	42.7	42.0
retention parameter a [mm]	-20	-15	-14	-10
retention parameter b [ ]	12.0	12.5	9.0	8.0
application atrazine [g/ha]	506	506	506	506
application terbuthylazine [g/ha]	492	492	492	492
bromide leaching soil columns:				
length of soil column [cm]	22.3	22.1	20.6	20.3
bulk density [g/cm^3]	1.31	1.31	1.33	1.31
total porosity [%]	50	51	49	49
field capacity [%]	43.6	43.7	44.7	44.0
retention parameter a [mm]	-20	-15	-70	-8
retention parameter b [ ]	12.0	12.5	6.0	12.0
application atrazine [g/ha]	89.3	89.3	89.3	89.3
soil-pesticide analyses:				
specific soil density [g/cm^3]	2.64	2.68	2.61	2.56
sat. effective porosity [%]	42.3	43.5	45.0	44.5
sat. dispersivity [cm]	0.6	1.5	0.2	1.5
sat. hydraulic conductivity [µm/s]	20.6	21.8	5.6	22.0
residual water content [%]	10.7	11.3	5.6	6.2
soil pH	6.1	5.4	5.1	7.0
organic carbon content [%]	2.22	1.40	1.23	0.66

K_d for terbuthylazine [l/kg]	5.8	3.6	1.7	0.7
K_d for atrazine[l/kg]	1.1	0.6	1.1	0.6
½ for terbuthylazine [days]	81	250	69	104
½ for atrazine [days]	56	143	44	

Fig. 2: Bromide (application: 10. day)
measured and simulated BTCs

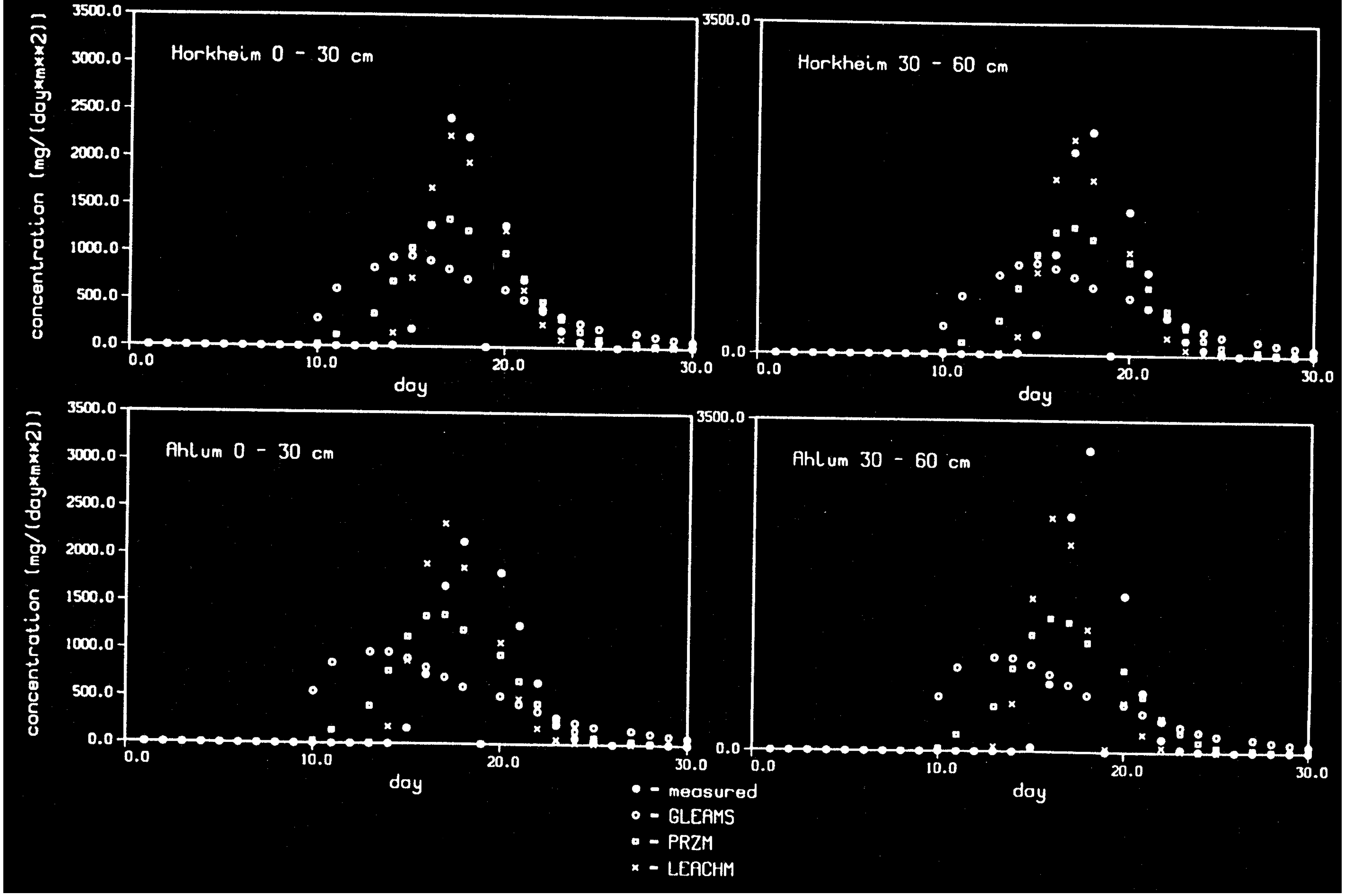


Fig. 3: Atrazine (application: 10. day)
measured and simulated BTCs

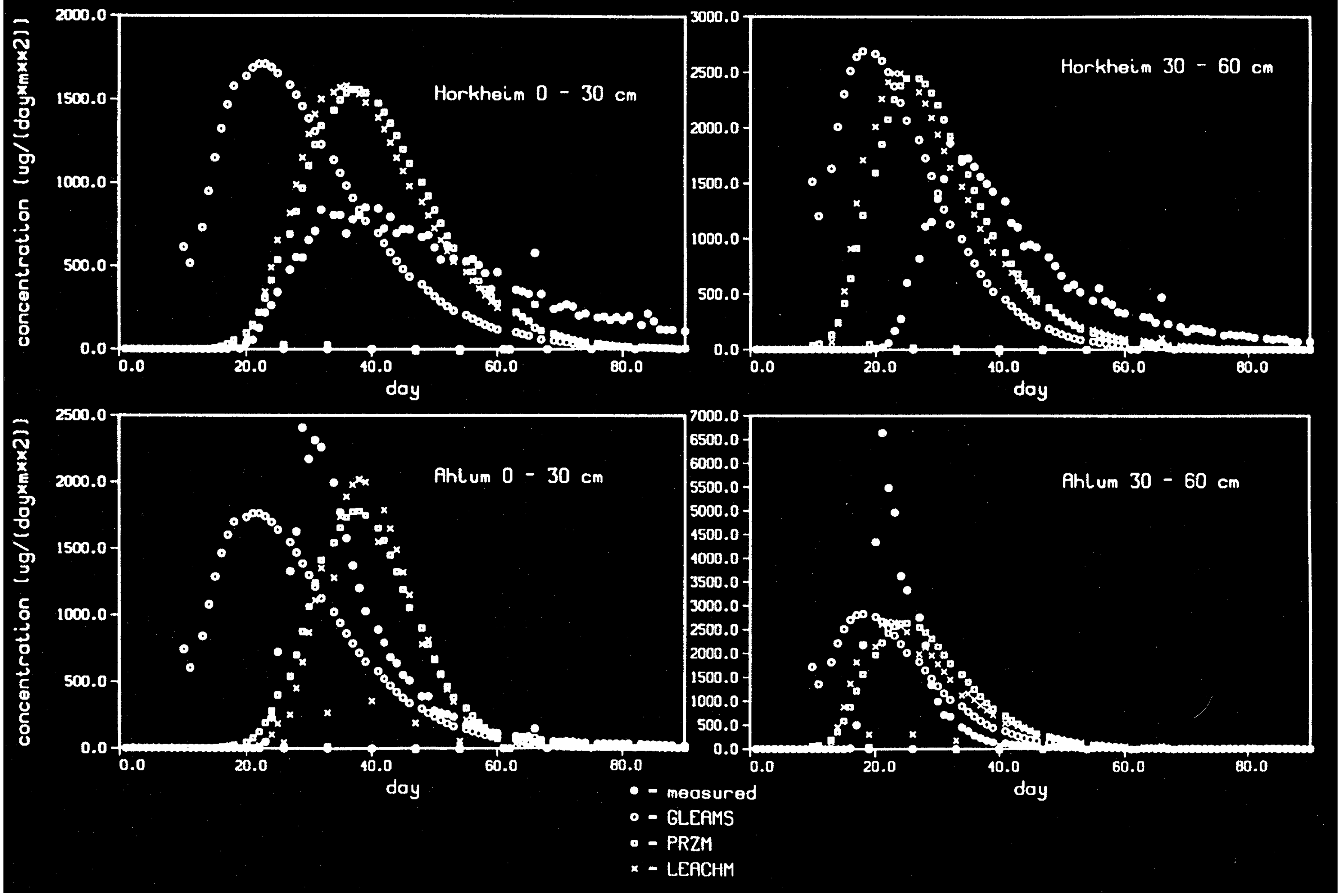
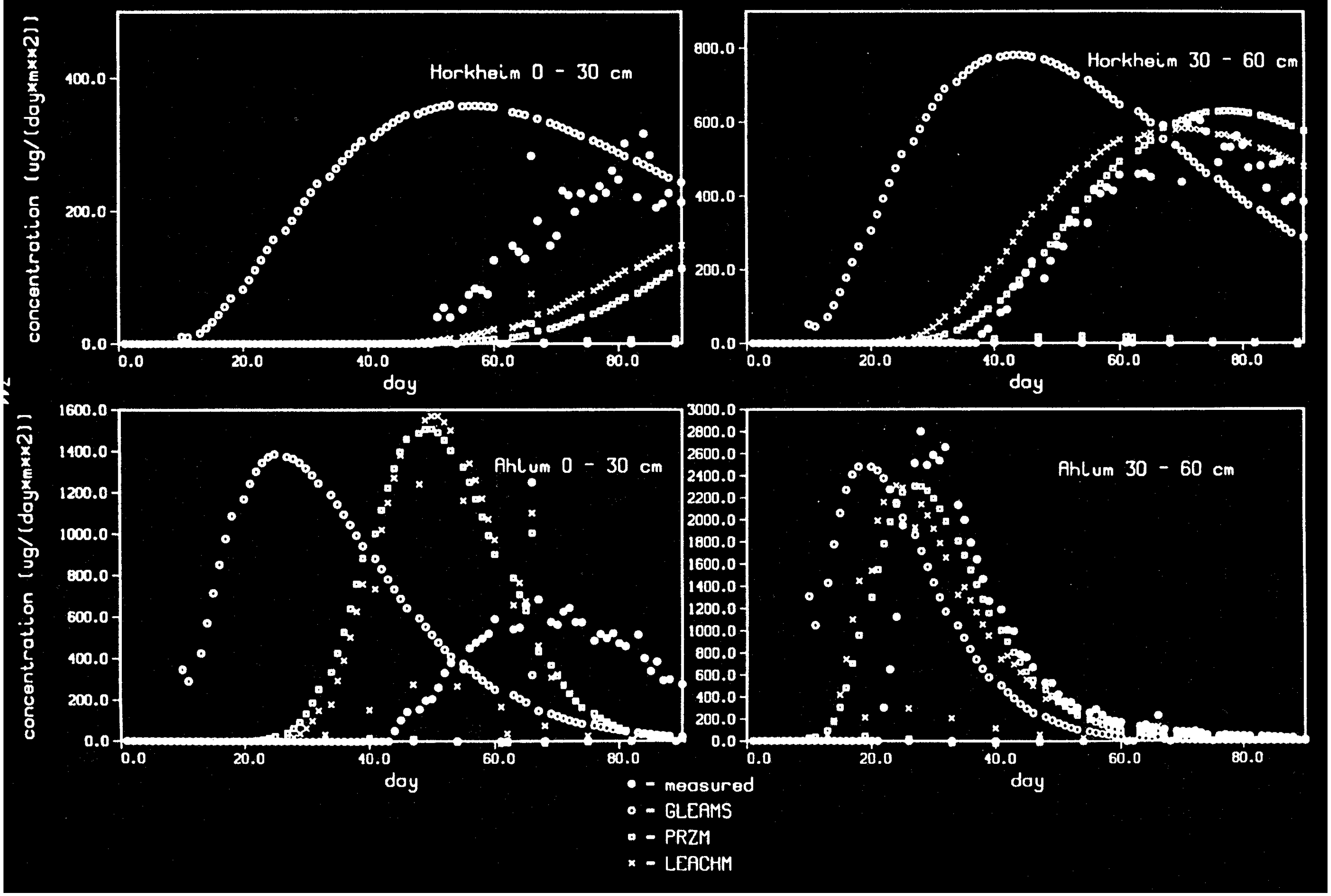


Fig. 4: Terbuthylazine (applic.: 10.day)
measured and simulated BTCs



PRZM estimates show close similarities to the results of LEACHM simulations. The close resemblance was mainly due to the fact that the two model concepts accurately simulated water flux and both models employed a finite difference scheme to solve the advection-dispersion equation. It is important, however, to understand that the advection-dispersion equations (8) of the two models are only identical for a steady-state flow regime with constant velocity where the dispersion coefficients remains a constant. Under transient flow conditions, the dispersion coefficient in LEACHM (eq. 11) is velocity-dependent.

PRZM and LEACHM simulations were significantly better than GLEAMS simulations, particularly in the case of the Horkheim soils, where breakthrough was relatively slow. Numerical dispersion was larger with PRZM than with LEACHM computations. The difference was significant only for fast transport, e.g. the bromide BTC simulations, which were computed with D = 0 (fig. 2). In these cases, numerical dispersion caused an underestimation of peak concentrations. LEACHM simulations corresponded well to the bromide BTCs.

Like GLEAMS, the two models failed to encompass the entire variety of experimental BTCs. Simulation of slow BTCs are characterized by overestimated peak concentrations (up to a factor two) and slightly underestimated peak arrival times (up to 30%), while fast BTCs were simulated with too much spread and lower peak concentrations. One should notice, however, that some simulated BTCs (terbuthylazine in Hk36 and Ah36, atrazine in Ah03) were very close to the measured BTCs and that in most cases the position of the BTCs were simulated rather accurate. The best estimates of total mass of pesticide leached after 80 days were obtained for fast BTCs (atrazine in Ah03 and Ah36, terbuthylazine in Ah36), with 2 to 7% error (GLEAMS: 11% to 26%). Mass error was up to 26% (GLEAMS: 35%) for other BTCs not including very slow BTCs with incomplete data (Terbuthylazine in Hk03, Hk36, and Ah03). In all cases estimated total solute mass was larger than measured.

The results of this first set of model predictions represent a situation, in which pesticide transport was predicted on the basis of site specific laboratory data. General criteria to judge the accuracy of such modeling efforts were reported by Hedden (in: Hern 1986, pp.81-101): Practical model applications require that uncalibrated simulation results for specific field sites are within a factor of two of measured field data. In this study, only PRZM and LEACHM simulations complied with such rigorous standards, and only by a small margin. Note, however, that many of the field related uncertainties (e.g. plant growth, evapotranspiration, runoff, erosion, soil heterogeneity) were negligible in the column experiments. We therefore expect that even PRZM and LEACHM simulations will not render the above mentioned accuracy if applied to field sites.

Model Prediction after Calibration

Calibration of two models (PRZM and LEACHM) was implemented by fitting the three most sensitive parameters K_d, $t_{½}$, and α. The objective of the calibration was to search for consistent differences between optimized and measured values and to assess the model concepts. Figure 5 and 6 show the results of the calibrated PRZM and LEACHM simulations. For comparison, calibrated K_{oc}, $t_{½}$, and α values are plotted against their measured values (fig. 7). GLEAMS simulations could not be calibrated due to strong smearing effects. Without a dispersion factor, the parameters K_d and $t_{½}$ proved to be insufficient to calibrate GLEAMS. GLEAMS' tipping bucket approach in both flow and transport computations caused immediate breakthrough after pesticide application, regardless of the choice of K_d.

After calibration, PRZM and LEACHM very accurately described all of the measured BTCs. The cumulative sum of daily sample concentrations with time was used to quantify the difference between measured and simulated breakthrough curves. The coefficient of variation for the calibrated curves varied from 2.4% to 7.9% (uncalibrated simulations: 12.5% to 320%). The results of PRZM and LEACHM simulations were similar.

Calibrated K_{oc} values were randomly distributed within a factor of two above and below the analytical values independent of soil sample or pesticide. In contrast, calibrated half-lives were consistently below the values from the degradation studies. The difference was within a factor of two (except terbuthylazine in Hk36). The range of calibrated Koc and half-life values partially reflected the uncertainty inherent to the measurement methods (Dibbern, personal communication). Thus the assumptions of linear, reversible, and instant adsorption and of first-order degradation seemed to be justified. However, significant deviations from the laboratory measurements were recorded for the calibrated dispersivity α, which is by definition a soil-specific, solute-independent parameter. Notice, that in all soil samples, except Ah03, calibrated α values differed widely for the three different solutes (terbuthylazine, atrazine, and bromide) (fig.7). During the calibration, α had obviously served as a fudge factor to also account for pesticide-specific reactions. In particular, nonlinear or nonequilibrium sorption processes may have caused additional spreading of the breakthrough curves, i.e. an increase of the observed dispersivity (Brusseau 1989).

CONCLUSION

The study has shown that all three models accurately simulate pesticide transport to a given depth within a factor of two, if soil column conditions closely match model assumptions (e.g. soil uniformity) and no vapor phase or plant related processes are considered. Only some of the GLEAMS estimates are less accurate. In addition, GLEAMS computations provided no practical estimates of BTC arrival times. All three models yielded conservative estimates with respect to the total mass of pesticide transport past the bottom of the soil column.

The quality of the simulation results depended only partially on the complexity of the model used. A pure cascade model concept proved to be adequate to describe a well-defined steady-state flow regime. But the approach performed relatively poor, when used for transport simulations (GLEAMS). Solving the physically-based advection-dispersion equation to compute solute transport (PRZM and LEACHM) led to significantly better results at the cost of computational effort. In terms of accuracy, the three models can be ranked in the order:

GLEAMS < PRZM < LEACHM

Fig. 5: Best fit to atrazine BTC

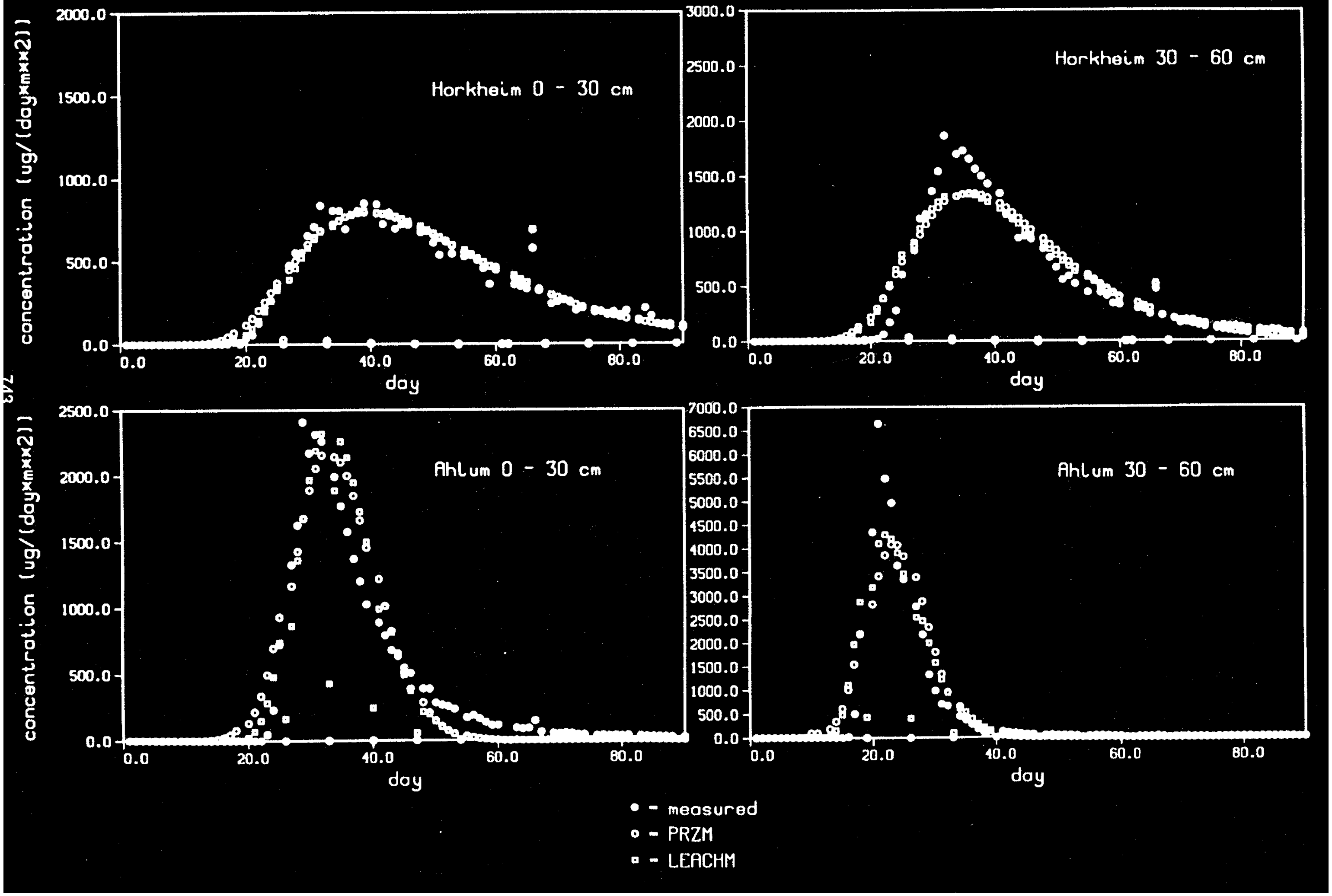


Fig. 6: Best fit terbuthylazine BTC

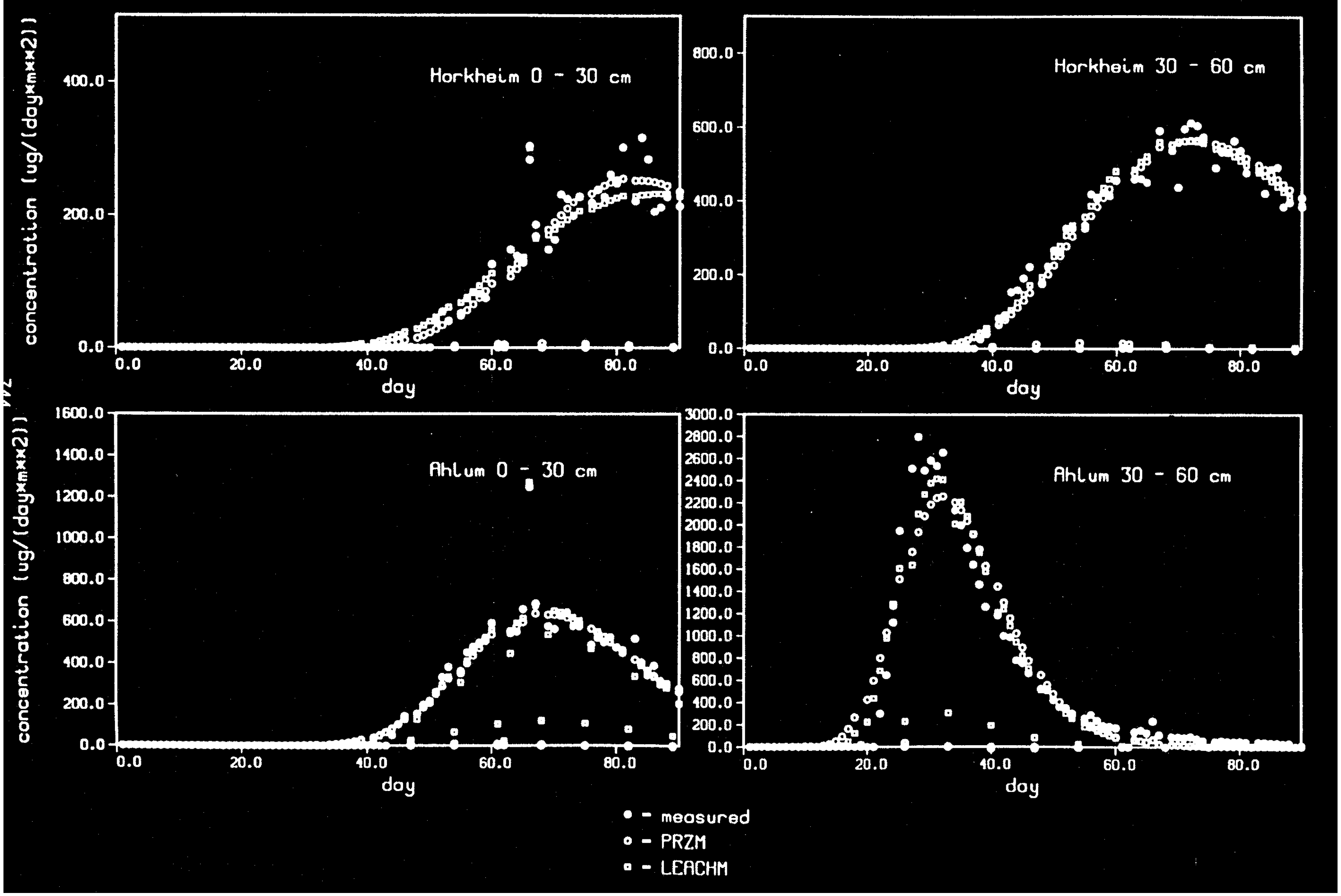
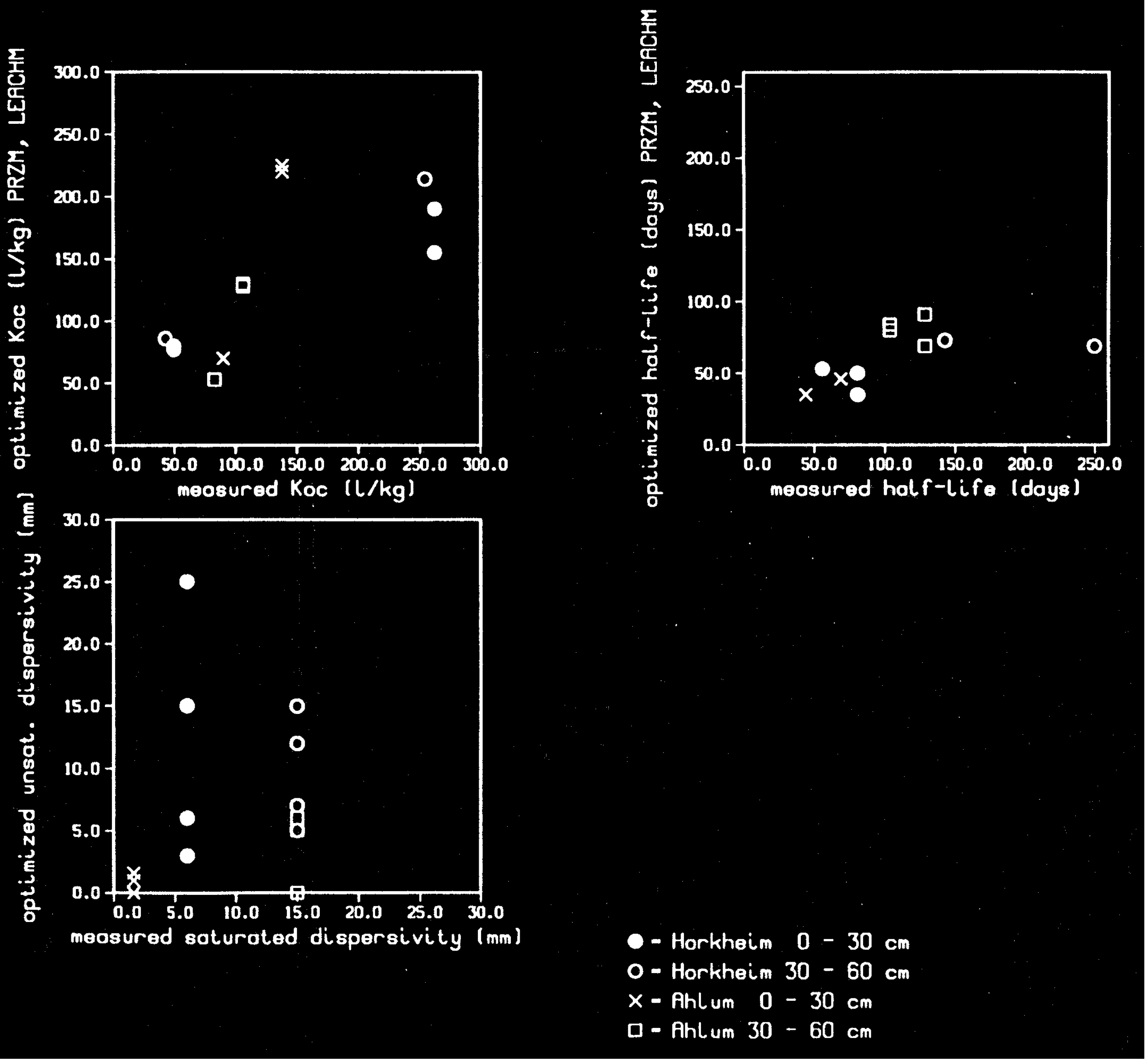


Fig. 7: Optimized versus measured parameters



PRZM differed little from the predictions of LEACHM in these experiments. However, the relative weakness of GLEAMS simulations clearly indicated that the incorporation of a physically well-based dispersion concept is important to obtain good modeling results. Under transient conditions LEACHM will provide far more flexibility than PRZM to accurately simulate dispersion processes because the dispersion coefficient itself is transient. Nevertheless, modeling the dispersion process has its limitations: Exact description of the dispersion process is of little advantage, if sorption and degradation simulations are not equally accurate. Our study has shown that nonideal sorption behaviour could play a significant role in atrazine and terbuthylazine transport.

The site specific measurements of all user-defined model parameters, in particular measurements of the distribution parameter K_d, were necessary to obtain acceptable simulation results. The study showed that K_{oc} values cannot always be used as soil-independent parameters.

Finally we emphasize that these results do certainly not reflect the accuracy of the models when applied to field situations.

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