

# Application of pesticide leaching models to the Vredepeel dataset II Pesticide fate

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## Abstract

The performance of nine deterministic, one-dimensional, dynamic pesticide leaching models with different complexity was evaluated using a field experiment with bentazone and ethoprophos on a humic sandy soil with a shallow groundwater table. All modelers received an extensive description of the experimental data. Despite this fact, the interpretation of the experimental data was ambiguous, leading to tremendous user-dependent variability of selected model inputs. Together with the fact that most modelers calibrated at least part of their model, the possibility for evaluating model concepts was limited. In the case of bentazone, most model predictions were within the 95% confidence intervals of the observations. In the case of ethoprophos, model performance was often poor due to the ignorance of volatilization, kinetic sorption and adaptation of the microbial population. Most models were calibrated using on-site measured data, limiting the possibility for extrapolation for policy-oriented applications. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Pesticide residues were found in groundwater all over Europe (Leistra and Boesten, 1989) and the USA (Hallberg, 1989). Agriculture is a dominant source of these pesticide residues. Although the environmental hazard associated with the observed environmental concentrations is poorly defined, it is generally accepted that leaching losses within agricultural fields should be minimized.

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The fate of pesticides in the soil is determined by a considerable number of processes, such as solute transport, degradation, sorption, plant-uptake, and volatilization. The interaction between these processes is complex and non-linear (Boesten, 1991; Tiktak et al., 1994b), making use of mechanistic pesticide fate models in quantitative groundwater management indispensable. The use of these models for registration purposes and regional scale assessments, however, is hampered by the shortage of sufficiently detailed experimental data to allow appropriate validation tests. The resulting low validation status of most pesticide leaching models is a critical issue. An aspect that has not received much attention in model evaluation is the level of variation in model outputs introduced by user-dependent subjectivity during derivation and selection of model input parameters (Brown et al., 1996; Boesten, 2000).

The main objective for the study presented in this paper was to evaluate and compare the ability of a number of well established pesticide leaching models to simulate the movement and distribution of two pesticides in the soil system. Specific attention was given to user-dependent subjectivity during derivation of model input parameters. The models were applied to a dataset collected from a field experiment in a humic sandy soils near Vredepeel, The Netherlands (Boesten and Van der Pas, 2000). This paper deals with the pesticide behavior part of the models, in an accompanying paper (Vanclooster and Boesten, 2000) the water flow and solute transport submodels are evaluated.

## 2. Materials and methods

### 2.1. The models

A total number of nine pesticide leaching models were considered in this comparison study (Table 1). All models were deterministic, dynamic, one-dimensional, multi-layer in their approach. All processes required for a proper description of pesticide fate were incorporated into the models. The models differed mainly in the complexity by which the various processes are modeled. This paper deals with the pesticide part of the models. Refer to Vanclooster and Boesten (2000) for details on water flow and solute transport.

In the simplest description of sorption, it is assumed that sorption is a reversible, linear, equilibrium process (GLEAMS, PRZM, MACRO and WAVE). In MACRO, the sorption sites are partitioned into a fraction that equilibrates with the macropores and another fraction that equilibrates with the soil matrix. The linear equilibrium approach requires only a few input parameters, i.e. the linear distribution coefficient ( $K_d$ ), or a combination of the organic matter content ( $f_{om}$ ) and the coefficient for distributing the substance over organic matter or organic carbon and the soil liquid ( $K_{om}$  or  $K_{oc}$ ). LEACHM and PESTRAS also assume equilibrium sorption, but these models consider non-linear (Freundlich) sorption. These models require one extra input parameter, i.e. the Freundlich exponent,  $n$ , to describe the non-linearity of the sorption isotherm. VARLEACH, PELMO and PESTLA also consider kinetic (non-equilibrium) sorption.

All models consider the degradation process to obey first-order kinetics. The most important input parameter is the degradation rate ( $r_d$ ) or the degradation half-life ( $DT_{50}$ ),

Table 1  
Overview of models used in this study

Subject	Model								
	VARLEACH v2.0	GLEAMS v2.1	PRZM-2 v2.0	PELMO v2.01	LEACHM v3.1	PESTLA v2.31	PESTRAS v3.1	MACRO v4.0	WAVE
Reference	Walker and Hollis (1994)	Leonard et al. (1987)	Mullins et al. (1992)	Klein, 1995	Hutson and Wagenet (1992)	Boesten and van der Linden (1991)	Freijer et al. (1996)	Jarvis (1991)	Vanclouster et al. (1995)
No. of modelers	3	3	2	3	2	3	1	2	1
Water flow	Capacity	Capacity	Capacity	Capacity	Richards	Richards	Richards	Richards	Richards
Pref. flow	No	No	No	No	No	No	No	Yes	Yes
Solute transport	Convective	Convective	CDE	CDE	CDE	CDE	CDE	CDE	CDE
Sorption	Linear equil. + kinetic	Linear equil.	Linear equil.	Freundlich equil. + kinetic	Freundlich equil.	Freundlich equil. + kinetic	Freundlich equil.	Linear equil.	Linear equil.
Degradation <sup>a</sup>	First-order, <i>T</i> dep.	First-order, <i>T</i> , pH dep.	First-order, <i>T</i> dep.	First-order, <i>T</i> dep.	First-order, <i>T</i> dep.	First-order, <i>T</i> , <i>z</i> dep.	First-order, <i>T</i> , <i>z</i> dep.	First-order, <i>T</i> dep.	First-order, <i>T</i> dep.
Plant-uptake	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Volatilization	No	Yes	No	No	Yes	No	Yes	No	No

<sup>a</sup> is soil water content, *T* is temperature, *z* is depth and dep. means 'dependent'.

which is usually allowed to vary with depth, soil water content and temperature (see Table 1).

Plant-uptake of pesticide is considered in all models except VARLEACH (In fact, VARLEACH does not consider the presence of crops at all). Plant-uptake is assumed to be passive, i.e. uptake is proportional to the transpiration rate and the pesticide concentration. Four out of nine models (PRZM, PESTLA, PESTRAS and MACRO) incorporate a ‘concentration stream factor’ to account for selective uptake.

Transport in the gas phase and surface volatilization is accounted for in LEACHM and PESTRAS. In these models, volatilization is assumed to occur through a thin surface layer. The driving force is the concentration gradient of pesticide across this layer, and the concentration of the pesticide in the atmosphere above the layer is assumed to be zero. Input data are the Henry’s law constant, the gas phase diffusion coefficient of the pesticide, and the surface resistance for volatilization.

## 2.2. Evaluation procedure

The models were compared with the observed total pesticide content profiles at three selected times (i.e. 103, 278 and 474 days after application; see Figs. 1 and 2). Using this information, the model predictions were mutually compared using a statistical performance indicator, which tries to express the agreement between model predictions and observations based on objective criteria. Various performance indicators exist (Loague and Green, 1991; Janssen and Heuberger, 1995) from which we choose the Modeling Efficiency (Vanclouster et al., 2000). The Modeling Efficiency indicates whether the model describes the data better than simply the arithmetic average of the observations. The optimal value is one. As indicated by Janssen and Heuberger (1995) results should be interpreted with care, and only a combination of statistical comparison and graphical representations is useful. In the graphs, the spread in the measurements was considered by plotting the lower and upper bounds of the 95% confidence intervals of the observations.

## 3. Results and discussion

### 3.1. Model parameterization

Tables 2 and 3 shows the range of pesticide dosages, sorption distribution coefficients and half-lives assumed by the various modelers. The range of parameter values are listed per model. Despite the fact that all modelers used the same description of the experimental data, the table shows tremendous user-dependent variability of the selected model inputs. Variability is highest for the half-life in the subsoil, and lowest for the sorption coefficient in the topsoil. A first examination of the list of model parameters did not show a relationship between the general experience of the modeler in deriving pesticide properties and the parameter values chosen. The range of model inputs observed amongst the three most experienced experts in the field of pesticide modeling was as high as the range of values listed in Tables 2 and 3.

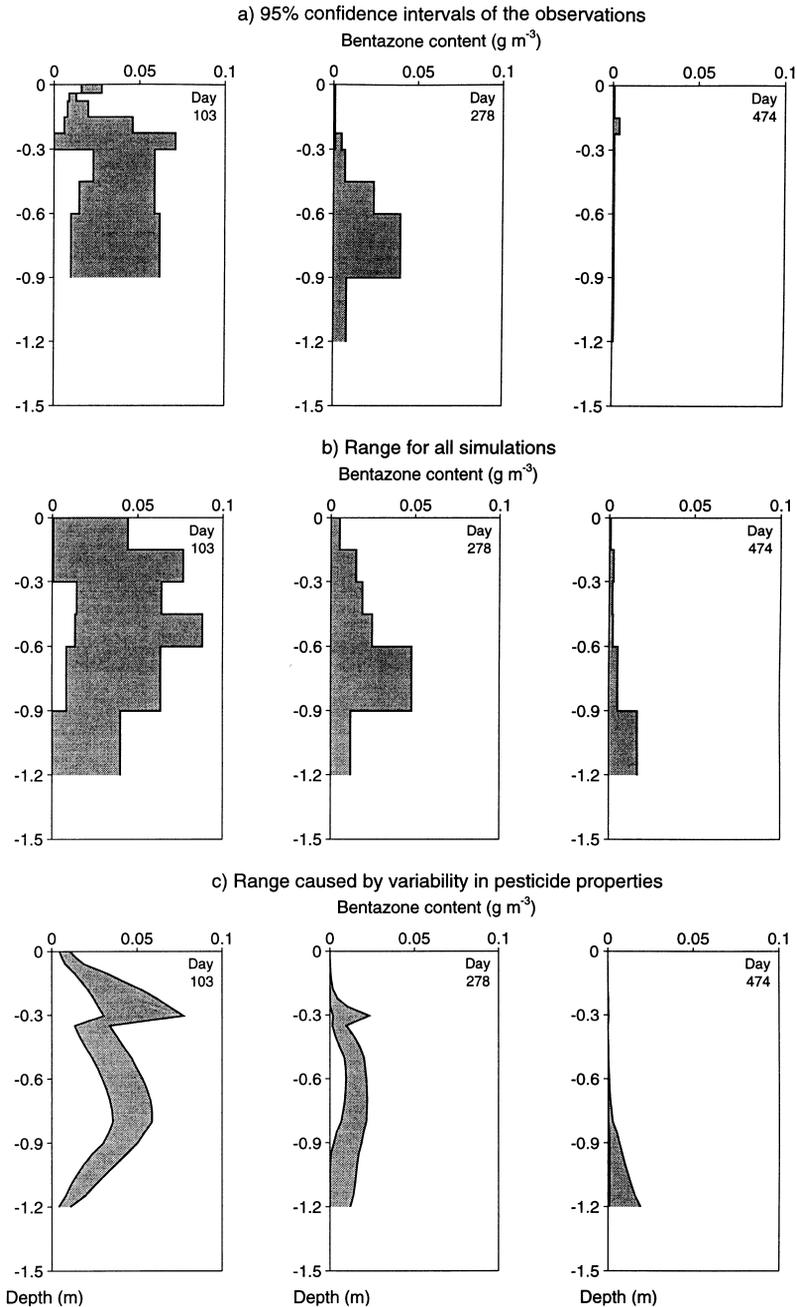


Fig. 1. Bentazone mass content as a function of depth at 103, 278 and 474 days after application: (a) 95% confidence intervals of observed contents, (b) full range of all simulations provided by the participants to the ring-test, (c) range resulting from user-dependent variability of half-life and the sorption coefficient, simulated with the PESTRAS model.

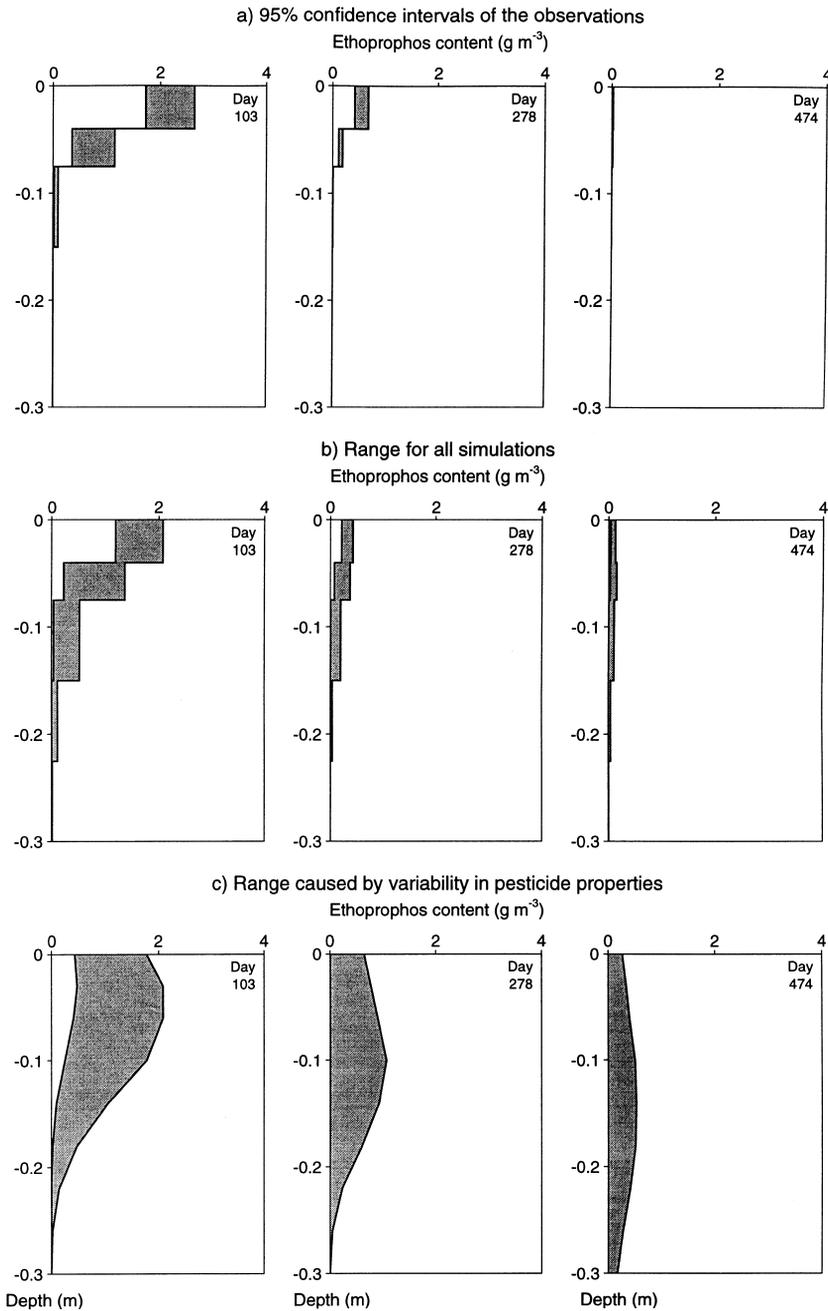


Fig. 2. Ethoprophos mass content as a function of depth at 103, 278 and 474 days after application: (a) 95% confidence intervals of observed contents, (b) full range of all simulations provided by the participants to the ring-test, (c) range resulting from user-dependent variability of half-life and the sorption coefficient, simulated with the PESTRAS model.

Table 2

Overview of major model inputs for bentazone showing the lowest and highest parameter values selected per model

Model	Dose (kg)	DT <sub>50</sub> (days) <sup>a</sup>		K <sub>F</sub> (l kg <sup>-1</sup> ) <sup>b</sup>		n (-) <sup>c</sup>
		0 cm	50 cm	0 cm	50 cm	
VARLEACH	0.73–0.80	37–78	56–2310	0.11–0.13	0.01–0.13	1.0–1.0
GLEAMS	0.73–0.80	20–50	20–100	0.10–0.10	0.10–0.10	1.0–1.0
PRZM-2	0.73–0.80	57–77	82–347	0.10–0.11	0.01–0.04	1.0–1.0
PELMO	0.80–0.80	50–71	100–500	0.09–0.11	0.01–0.03	0.92–1.0
LEACHM	0.80–0.80	37–50	56–100	0.09–0.13	0.04–0.13	1.0–1.0
PESTLA	0.63	88	10 <sup>6</sup>	0.11	0.02	0.82
PESTRAS	0.73	81	13 000	0.13	0.01	0.87
MACRO	0.63–0.80	36–86	200–1630	0.11–0.11	0.02–0.02	1.0–1.0
WAVE	0.63	20	10 <sup>6</sup>	0.10	0.004	1.0

<sup>a</sup> Degradation half-life of bentazone at 10°C and field-capacity.

<sup>b</sup> Freundlich coefficient.

<sup>c</sup> Freundlich exponent.

Generally, there are three reasons for the extreme user-dependent variability of model inputs, i.e. (i) calibration of pesticide properties, (ii) use of literature data instead of measured data, and (iii) ambiguity in the interpretation of laboratory data. The first two in fact reflect different modeling strategies.

Some modelers calibrated pesticide properties. They justified this by the fact that the laboratory experiments did not necessarily represent processes occurring under field conditions. The microbial population, e.g., may have been disturbed during sampling, so that field-degradation rates were higher than laboratory-degradation rates. Some modelers believed that this was especially true for the subsoil where micro-aerobic to anaerobic conditions occurred. This explains why the range of half-lives is higher for the subsoil

Table 3

Overview of major inputs for ethoprophos showing the lowest and highest parameter values selected per model

Model	Dose (kg)	DT <sub>50</sub> (days) <sup>a</sup>		K <sub>F</sub> (l kg <sup>-1</sup> ) <sup>b</sup>		n (-) <sup>c</sup>
		0 cm	50 cm	0 cm	50 cm	
VARLEACH	3.0–3.35	132–219	198–533	2.7–3.6	0.2–2.7	1.0–1.0
GLEAMS	3.0–3.35	25–90	76–200	3.2–3.6	3.2–3.6	1.0–1.0
PRZM-2	3.0–3.35	17–157	35–292	1.8–4.3	0.1–0.2	1.0–1.0
PELMO	1.3–3.35	153–166	300–319	3.5–4.3	0.2–1.5	0.86–0.87
LEACHM	1.3–3.35	132–153	198–300	2.7–3.5	1.5–2.7	0.8–1.0
PESTLA	1.3	196	466	4.2	0.9	0.87
PESTRAS	3.35	212	537	3.2	0.2	0.81
MACRO	2.7–2.7	102–231	153–435	2.4–6.0	0.1–0.3	1.0–1.0
WAVE	1.3	83	270	9.0	0.16	1.0

<sup>a</sup> Degradation half-life of ethoprophos at 10°C and field-capacity.

<sup>b</sup> Freundlich coefficient.

<sup>c</sup> Freundlich exponent.

than for the topsoil. The second reason for user-dependent variability is that some modelers used generic (literature) data for pesticide properties. They stated that fair statements about the predictive power of a model for pesticide registration purposes could only be made if the model was parameterized using generic data. The most important reason for user-dependent variability is that the interpretation of the experimental data is ambiguous. Some examples follow in the remainder of this chapter; however, other problems in data-derivation exist.

### 3.1.1. Pesticide dosage

Tables 2 and 3 shows that different application rates were used. Modelers used one of the following methods to calculate the pesticide dose (figures between brackets are those for bentazone):

- calculation based on the concentration of the chemical in the spraying solution, the water flow rate and the speed of the spraying device ( $0.80 \text{ kg ha}^{-1}$ ),
- estimation based on the mass recovered directly after application ( $0.63 \text{ kg ha}^{-1}$ ), or
- calculation based on the mass recovered directly after application, but with correction for analytical recovery ( $0.73 \text{ kg ha}^{-1}$ ).

In the case of ethoprophos, some modelers used the dose recovered after 23 days to account for the rapid volatilization after application. From the models reviewed in this paper, only PESTRAS, GLEAMS and LEACHM contain a description of surface volatilization.

### 3.1.2. Pesticide sorption parameters

Adsorption isotherms were determined at 5 and 15°C (bentazone) and 5 and 25°C (ethoprophos) with soil sampled from the topsoil (Boesten and Van der Pas, 2000). Subjectivity was introduced because one could either fit a sorption isotherm to the low-temperature sorption points, the high-temperature sorption points, or even fit all sorption points simultaneously. Further subjectivity was introduced by the possibility of using different fitting procedures. Tiktak et al. (1998), e.g., showed that non-linear curve fitting of the original data yielded different results than linear regression of log-transformed data (Table 4). A final point of concern is how modelers parameterized their sorption isotherms for the subsoil. Most modelers used the  $K_{\text{om}}$  concept in which it is assumed that the distribution coefficient is proportional to the organic matter content. Some modelers,

Table 4  
Freundlich parameters after linear fitting of log-transformed data and non-linear curve fitting of the original data

Parameter	Ethoprophos				Bentazone			
	Log-transformed		Non-linear		Log-transformed		Non-linear	
	5°C	25°C	5°C	25°C	5°C	15°C	5°C	15°C
$K_{\text{om}} (\text{kg}^{-1})^{\text{a}}$	59	86	63	90	2.8	2.6	2.8	2.5
$1/n$	0.83	0.90	0.81	0.88	0.90	0.86	0.91	0.90
$r^2$	0.99	0.99	0.98	0.99	0.99	0.99	0.98	0.99

<sup>a</sup> Calculated from  $K_{\text{F}}$  using the organic matter content of the topsoil.

Table 5  
Half-life under reference conditions and temperature dependence of transformation using different fitting procedures

Parameter	Ethoprophos		Bentazone	
	ln-transformed	Non-linear	ln-transformed	Non-linear
$E_a$ (kJ mol <sup>-1</sup> ) <sup>a</sup>	67	67	90	121
$\gamma^c$	0.094	0.094	0.126	0.170
DT <sub>50</sub> , A layer (days) <sup>b</sup>	105	83	28	16
DT <sub>50</sub> , B layer (days) <sup>b</sup>	186	210	2610	1880
DT <sub>50</sub> , C layer (days) <sup>b</sup>	146	125	27	14

<sup>a</sup> Molar energy of activation in Arrhenius equation.

<sup>b</sup> At  $T = 20^\circ\text{C}$ .

<sup>c</sup>  $\gamma$  = Exponent in Arrhenius equation.

however, decided to use one distribution coefficient for the entire soil profile (see Tables 2 and 3).

### 3.1.3. Degradation

The rate of transformation in the topsoil was measured in the laboratory at 5 and 15°C in the case of bentazone and 5, 15 and 25°C in the case of ethoprophos. Most modelers fitted first-order rate degradation constants for the individual temperatures, after which the temperature dependence of degradation was calculated; however, those people who used a model in which the half-life was independent of soil temperature usually decided to fit the 5 and 15°C degradation points only. As shown by Tiktak et al. (1998), the calculated half-lives and the molar activation energy in the Arrhenius equation were strongly affected by the fitting procedure (Table 5). This is caused by the large scatter in the data-points as shown by Boesten and Van der Pas (2000): In the case of linear regression on ln-transformed data, lower points are given relatively more weight, whereas the opposite is true for non-linear curve fitting. The value of the molar energy of activation for bentazone is outside the range of 50 experiments reviewed by Boesten (1986) indicating that the temperature of 5°C chosen as the lower range of temperatures in the transformation experiment may have been outside the range for which the Arrhenius equation applies. Some modelers decided not to use this high activation energy and used model defaults, introducing yet another source of user-dependency. In the case of bentazone, further differences resulted from the fact that the laboratory-degradation rates did not exactly meet the assumption of first-order rate kinetics. Some modelers fitted the rate constant to the initial, faster, degradation phase. Some models (e.g., MACRO) assume different degradation half-lives of pesticide in the soil solution and pesticide sorbed at the soil solid phase. As the experiments only consider the overall degradation rates, the derivation of such figures added additional subjectivity.

Subsoil degradation studies were carried out for the 50–100 and 100–200 cm soil layers. The degradation studies suggested very low degradation rates for the 50–100 cm soil layers, while the degradation rates for the deepest soil layer were almost as high as the topsoil degradation rates (Table 5). Not all modelers trusted the experiments, so they decided to keep degradation constant with depth or they used default values for the depth

Table 6

Modeling Efficiency for predictions of bentazone and ethoprophos in the soil profile showing the worst and the best runs for each model

Model	Modeling Efficiency			
	Bentazone		Ethoprophos	
	Worst	Best	Worst	Best
VARLEACH	−5.7	−1.0	−1.0	0.0
GLEAMS	−1.1	0.5	0.3	0.7
PRZM-2	0.5	0.7	−4.5	0.4
PELMO	−0.7	−0.4	−0.7	0.9
LEACHM	−4.5	0.8	−1.0	−0.4
PESTLA	–	−0.1	–	0.8
PESTRAS	–	0.5	–	0.2
MACRO	0.6	0.7	0.8	0.9

dependence of transformation. However, independent incubation studies with 2,4D [(2,4-dichlorophenoxy)-acetic acid] and acetate, carried out after most modelers already made their model runs, also suggested lower activity in the 50–100 cm soil layer.

### 3.2. Model performance for bentazone

Observed and simulated bentazone concentration profiles at 103, 278 and 474 days after application are shown in Fig. 1, Table 6 shows the range of Modeling Efficiencies per model. The second row of graphs in Fig. 1 shows the range for all simulations, the third row is added to show the sensitivity of the simulated concentration profiles to user-dependent subjectivity in the derivation of the degradation half-life and the sorption coefficient. For this purpose, simulations were carried out with the half-life and sorption coefficient set at the average value  $\pm 2$  times the standard deviation. The model PESTRAS was used for this purpose. The average half-life at 10°C derived from the laboratory experiments was 74 days with a coefficient of variation of 42%, the average sorption coefficient was 0.11 dm<sup>3</sup> kg<sup>−1</sup> with a coefficient of variation of 14% (Boesten, 2000). Fig. 1b shows that there is considerable variation in the predicted concentration profiles, and a considerable part of this variation could be caused by user-dependent subjectivity during the derivation of model inputs (Fig. 1c).

Table 6 shows that the performance for the same model varied amongst users. In line with the general conclusions drawn from Fig. 1c we can state that this user-dependency of modeling is most likely caused by subjectivity during derivation of model inputs. The best Modeling Efficiency was generally found by those users who allowed pesticide properties to be calibrated. This is most striking in the case of VARLEACH and GLEAMS, where one of the users calibrated the degradation half-life and sorption coefficients, while the others did not.

User-dependent variability of model inputs limits the possibility for selecting the best model in terms of ability to reproduce the observed concentration profiles. Consider the following example. Vanclooster and Boesten (2000) evaluated the models with respect to

Table 7

Mass balance<sup>a</sup> of bentazone as a fraction of the applied dose for a selection of models

	Mass balance (% of applied bentazone) <sup>b</sup>					
	$f^{vol}$	$f^{tran}$	$f^{upt}$	$f^{sys}$	$f^l$	$f^{err}$
LEACHM	0.0	88.0	0.0	4.1	6.9	1.0
MACRO	0.0	65.2	0.0	6.8	28.0	0.0
PESTLA	0.0	37.1	28.0	6.7	28.2	0.0
PESTRAS	0.0	36.2	23.3	10.1	30.4	0.0
PRZM-2	0.0	47.0	0.0	10.0	43.0	0.0
WAVE	0.0	83.0	0.0	3.0	10.0	4.0

<sup>a</sup> Calculated for the end of the experiment and for the upper meter of the soil profile.

<sup>b</sup>  $f^{vol}$  is the fraction volatilized;  $f^{tran}$  the fraction transformed;  $f^{upt}$  the fraction taken up;  $f^{sys}$  the fraction left in system;  $f^l$  the fraction leached from the upper meter of the soil profile and  $f^{err}$  the numerical mass balance error.

the water flow and solute transport components. An important conclusion from their comparison was that the Richards' models performed better than the capacity type of models. As bentazone is a mobile component it is to be expected that Richards' models also perform better for the pesticide part of the model. This, however, cannot be concluded from Table 6. For example, the Modeling Efficiency for PRZM-2 and GLEAMS is good while the Modeling Efficiency for PESTLA is negative. This is a typical example of the fact that 'model-error' (capacity models could not describe water- and solute-transport) can be cancelled out by 'parameter error' (a reasonable value for the Modeling Efficiency of GLEAMS could only be obtained after calibration of pesticide properties).

Despite the problems with data-derivation, all models and the observations indicated significant transport of bentazone; however, the magnitude of the leaching differed considerably (Table 7). Tiktak et al. (1998) calculated a maximum concentration of bentazone in the 1–2 m soil layer of  $15 \text{ g l}^{-1}$ , which is approximately 150 times the EU-drinking-water standard. Table 7 shows that there was no agreement about plant-uptake rates. A number of models did not include a module for pesticide uptake. Modelers using a model lacking a routine for pesticide uptake usually lumped pesticide uptake and transformation resulting in high degradation rates. The Dutch models PESTLA and PESTRAS calculated that a significant fraction of the applied bentazone was taken up. However, as bentazone is an ionic substance, parameter values for bentazone uptake are highly uncertain. Tiktak et al. (1998) showed that with the observed atypical depth dependence of degradation, an important fraction of the applied bentazone disappeared from the 1–2 m soil layer by transformation under micro-aerobic to anaerobic conditions. Anaerobic transformation is a key process in the prediction of the risk of contamination of drinking-water wells by pesticides, so research on transformation under anaerobic conditions is required.

### 3.3. Model performance for ethoprophos

The observations indicate a rapid decrease of ethoprophos directly after application (Fig. 3). This fast decrease stops after the first rainfall, and almost 60% of the applied

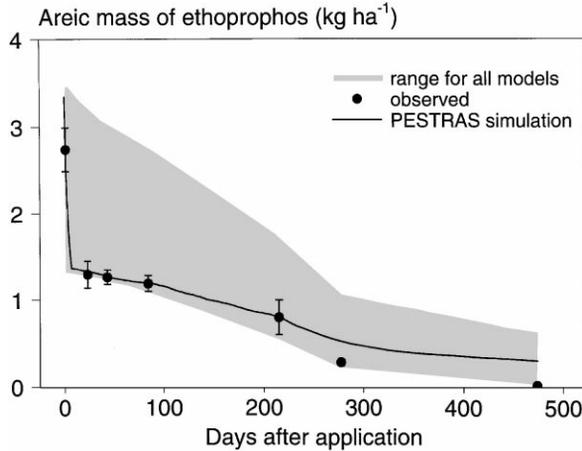


Fig. 3. Areic mass of ethoprophos as a function of time.

pesticide has then disappeared. The initial decrease is due to surface volatilization of the applied chemical, and could only be reproduced by the PESTRAS model (Fig. 3). However, most models do not contain a description of surface volatilization, and can therefore not deal with this initial decline. Modelers used the following methods to avoid this problem: (i) use of high degradation rates directly after application, and (ii) use of a lower pesticide dosage of  $1.33 \text{ kg ha}^{-1}$ , which is the amount recovered at 23 days after pesticide application. Although it is thus possible to describe the fate of ethoprophos during later stages of the experiment, it is clear that a proper description of surface volatilization is required for surface applied, moderately volatile or volatile pesticides ( $K_H > 10^{-5}$ ). The PESTRAS model did contain a module for surface volatilization, but the most important parameter governing volatilization (the surface resistance,  $R_v$ ) could only be obtained by calibration. Moreover, as the surface resistance is strongly dependent upon the atmospheric conditions after application (Jury et al., 1990; Freijer et al., 1996), predictions of surface volatilization remain too uncertain to be used for pesticide registration purposes or regional scale modeling (Tiktak et al., 1998).

Both the observations and the model predictions indicate that there was no ethoprophos below 0.3 m depth during the experiment (Fig. 2 a and b), so the models were conclusive about the leaching potential of ethoprophos (which is negligible). Nevertheless, the majority of models slightly overestimated the movement of ethoprophos (model results were outside the 95% confidence intervals), caused by ignorance of kinetic sorption (Ma et al., 1996). Results from long-term sorption experiments indeed confirmed that the distribution coefficient increased with time (Boesten and Van der Pas, 2000). Some modelers tried to imitate kinetic sorption by using a higher distribution coefficient. They indeed succeeded to calibrate the center of mass of pesticide residues in the soil profile, but they did not well describe the tail of the ethoprophos profile. The latter is significant from a pesticide registration point of view, as kinetic sorption may result in long-term leaching of pesticides at low concentrations (Pignatello and Huang, 1991; Wagenet and Hutson, 1996). After the initial volatilization phase, the areic-mass observations still

Table 8

Mass balance<sup>a</sup> of ethoprophos as a fraction of the applied dose for a selection of models

	Mass balance (% of applied bentazone) <sup>b</sup>					
	$f^{vol}$	$f^{tran}$	$f^{upt}$	$f^{sys}$	$f^l$	$f^{err}$
LEACHM	0.0	89.8	0.0	1.3	0.0	8.9
MACRO	0.0	57.0	0.0	39.0	0.0	4.0
PESTLA	0.0	75.2	1.5	23.3	0.0	0.0
PESTRAS	59.2	29.9	1.0	9.0	0.0	0.0
PRZM-2	0.0	75.0	0.0	25.0	0.0	0.0
WAVE	0.0	94.0	0.0	5.0	0.0	1.0

<sup>a</sup> Calculated for the end of the experiment and for the upper meter of the soil profile.<sup>b</sup> See Table 7 for an explanation of symbols.

show a two-phase behavior: From 214 days after applications onwards, pesticide dissipation accelerates (Fig. 3). As degradation is the most important loss pathway during the later stages of the experiment (Table 8), it can be stated that this is most probably caused by accelerated degradation due to adaptation of the microbial population. This was also found by Smelt et al. (1987) who found higher rates of transformation from annually treated fields compared with soils not previously treated. No single model was able to deal with this process, indicating that the first-order representation of degradation is not sufficient in this particular case.

The third row in Fig. 2 shows the effect of user-dependent variability of pesticide properties on ethoprophos concentration profiles. The average half-life at 10°C was 172 day with a coefficient of variation of 32%. For the sorption coefficient, these figures amounted to 3.4 dm<sup>3</sup> kg<sup>-1</sup> and 21% (Boesten, 2000). Fig. 2 shows that the variation in concentration profiles caused by user-dependent variability is higher than the variation of all simulations. This is caused by the fact that a number of modelers calibrated their model, so that the effect of variation of model inputs is partly cancelled out.

#### 4. Summary and conclusions

Within this study the performance of the pesticide fate part of nine well established pesticide leaching models was evaluated using a dataset collected on a humic sandy soil with a shallow groundwater table. The models were deterministic, dynamic, one-dimensional, multi-layer in their approach, and differed mainly in the complexity by which the various processes are modeled.

All modelers received an extensive description of the experimental data. Despite this fact, no single model run was parameterized in the same way. The most important reason for user-dependent variability of model inputs was that the interpretation of the experimental data was ambiguous. Subjectivity in deriving model inputs should be reduced when the models are to be used for registration purposes, so it is an important task for the modeling community to provide policy-oriented users with strict guidelines and additional tools for deriving model inputs.

The tremendous range in model inputs used by the modelers hampered the possibility for evaluating model concepts. This was enhanced by the fact that only three pesticide profiles were available for evaluation, so that the identifiability of model parameters was limited. Future studies on comparison of model concepts could use input mapping (Rose et al., 1991) and consider the effect of model complexity on parameter identifiability (Van der Perk, 1997). Evaluation of model concepts themselves is bound to be most successful when using one model in combination with a library of modules with different complexity of the included process descriptions (Tiktak et al., 1994a).

All models and the experimental data were conclusive with respect to the leaching potential of the two pesticides considered. The models indicated significant transport of bentazone to the 1–2 m soil layer, whereas the transport of ethoprophos below 0.3 m depth was negligible. Nevertheless, the magnitude of the simulated concentrations differed strongly between the models. In the case of bentazone, most model predictions were within the 95% confidence interval of the observations, but calibration was often necessary to accomplish this. This limits the general applicability of the models when used for pesticide registration purposes or regional scale modeling. This problem becomes even more serious when generic (literature) data are used for model parameterization, and this is usually the practice in policy-oriented applications. The accumulation of ethoprophos, e.g., was underestimated by a factor 7 when generic pesticide properties were used (Tiktak et al., 1998). It is an important task for modelers to provide decision makers with this kind of uncertainty (Loague and Corwin, 1996; Tiktak et al., 1998).

Despite the above mentioned problems with parameter identifiability, some general conclusions about model concepts could be drawn

- Almost 60% of the applied ethoprophos disappeared by surface volatilization, so models lacking a module for surface volatilization were not successful in describing the fate of this pesticide.
- The transport of ethoprophos was overestimated by models not dealing with kinetic sorption.
- Degradation of ethoprophos could reasonably be described using first-order kinetics until 214 days after applications. From that day onwards, degradation in the field was faster than predicted by the models probably due to adaptation of the microbial population.
- The depth-dependence of transformation for bentazone was atypical. Almost 30% of the applied bentazone leached below 1 m depth, and 20% disappeared from the 1–2 m soil layer by transformation under micro-aerobic to anaerobic conditions (Tiktak et al., 1998). Anaerobic transformation is a key process in predicting the risk of contamination of drinking-water wells.

Future research should be directed towards solving these problems. However, caution must be taken not to fall into the trap of building new model versions that contain a lot of parameters which cannot be derived from experimental data as the applicability of such models for regional scale applications is limited. Finding the balance between model complexity and parameter identifiability is also a challenge for future model developments (Loague and Corwin, 1996).

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