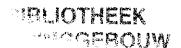Validation of the PESTLA model: Evaluation of the validation statuses of the pesticide leaching models PRZM-1, LEACHP, GLEAMS, and PELMO

Validation of the PESTLA model: Evaluation of the validation statuses of the pesticide leaching models PRZM-1, LEACHP, GLEAMS, and PELMO

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ABSTRACT

Bosch, H. van den, and J.J.T.I. Boesten, 1995. *Validation of the PESTLA model: Evaluation of the validation statuses of the pesticide leaching models PRZM-1, LEACHP, GLEAMS, and PELMO.* Wageningen (The Netherlands), DLO Winand Staring Centre. Report 83. 60 pp.; 1 Fig.; 4 Tables; 39 Refs.

The validation statuses of the pesticide leaching models PRZM-1, LEACHP, GLEAMS and PELMO were assessed by literature study. The required range of validity included all the situations in which pesticides are applied in Dutch agriculture and horticulture. The models should predict pesticide leaching to groundwater at concentration levels of some 0.1 µg/l based on laboratory-measured sorption and transformation rate parameters. All the available model tests were reviewed and their soundness and relevance classified. If the test was sound, model performance was analysed. Validation statuses of the models were low to very low, considering the required range of validity and the results of the available tests.

Keywords: concentration level, groundwater, range of validity, soil, sorption rate, transformation rate

The DLO Winand Staring Centre is continuing the research of: Institute for Land and Water Management Research (ICW), Institute for Pesticide Research, Environment Division (IOB), Dorschkamp Research Institute for Forestry and Landscape Planning, Division of Landscape Planning (LB), and Soil Survey Institute (STIBOKA).

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Preface

This literature study was carried out in the framework of the project 'Validation of PESTLA', carried out as a combined effort of the DLO Winand Staring Centre (SC-DLO) and the National Institute of Public Health and Environmental Protection (RIVM) by order of and for account of the Dutch Ministry of Agriculture, Nature Management and Fisheries and the Dutch Ministry of Housing, Physical Planning and Environment. The study was actuated by the question whether other models than PESTLA would be useful for the assessment of pesticide leaching to groundwater, as described by the Long-term Crop Protection Plan of the Dutch government.

This report is one of a series of reports that evolved from the project. The other reports present (i) definitions and the objectives of the project and the selection of the procedure used to assess the validation status of PESTLA (Boekhold et al., 1993a), (ii) tests of PESTLA against results of field experiments (Boekhold et al., 1993b; Van den Bosch and Boesten, 1994), (iii) a comparison of results of calculations with PESTLA against results of calculations with other pesticide leaching models (Beusen et al., 1995) and (iv) a final report that summarizes all previous reports (Van der Linden et al., 1995).

Summary

This study attempts to assess the validation status of a number of models for pesticide leaching. The status is assessed in the context of their possible use in the registration in the Netherlands as described in the Long-term Crop Protection Plan. This implies that a model should be able to simulate accurately pesticide leaching to groundwater at concentration levels in the order of 0.1 µg dm^{-3} using laboratory data on pesticide/soil interactions. The required range of validity embraces all pesticide applications in Dutch horticulture and agriculture.

Validation status is defined as the extent to which a model has successfully been validated within its range of validity. The concept of validation status is operationalized by linking it to the probability that the model will result in successful predictions within its range of validity. So to assess the validation status we need a population of model tests from which estimates for this probability can be derived.

Firstly, a number of existing leaching models were briefly reviewed. Based on this review and on the availability of model tests, the models PRZM-1, LEACHP, GLEAMS and PELMO were selected for further study. The validation status of each model was assessed by considering all available model tests. To evaluate the model tests the concepts 'soundness' and 'relevance' were introduced. At low leaching levels all models considered are very sensitive to the half-life (DT$_{50}$) and the organic-matter/water distribution coefficient (K$_{om}$). Therefore a model test was defined to be sound only if site-specific values for these parameters were obtained from laboratory experiments. The relevance of a particular study was assessed by comparing soil properties, hydrological conditions, crops and weather to those in the Netherlands and by checking whether all important processes were included in the test. Another aspect of the relevance is the concentration level at which the models were tested. In view of the importance of this aspect it was treated separately. The concentration of the pesticide in the solution deeper in the soil should be in the order of 0.1 to 1 µg dm^{-3}, because in the Netherlands the critical concentration level for groundwater is 0.1 µg dm^{-3} for a single pesticide and 0.5 µg dm^{-3} for the total concentration of all pesticides. If a model test was sound, the model performance was analyzed using the criteria that the penetration depth of the calculated peak concentration and the calculated peak concentration should be within a factor of 2 of the measured values.

Twelve tests of PRZM-1 were found, nine of which are described in detail (the three not considered in detail were either not sound or not relevant). Five of the nine tests were not sound. Two tests were moderately sound (implying that either K$_{om}$ or DT$_{50}$ was derived from site-specific measurements in the laboratory) and two tests were sound. Three of the four sound and moderately sound tests were relevant or moderately relevant. In these three tests the concentration level ranged between 10 and 200 µg dm^{-3} which is much higher than the critical level of 0.1 µg dm^{-3}. In all cases the depth of the peak concentration was overestimated by PRZM-1, but the calculated values were within a factor of two of the measured values. The calculated height of the peak concentration was always within a factor of two of the measured

value. Based on the above information the validation status of PRZM-1 is considered to be low in the context of our study.

Three tests of LEACHP were found. Two tests were sound and one was moderately sound. One test was relevant, one moderately relevant and one not relevant. In the studies the concentration level ranged between 10 and 5000 μg dm^{-3}. In two tests the calculated depth of the peak concentration was within a factor of two of the measured depth. In all cases the calculated height of the peak concentration was within a factor of two of the measured value. So LEACHP explained well the movement of pesticides in two (moderately) sound and (moderately) relevant tests conditions. The evaluations were carried out at concentration levels that were much higher than the critical level. Therefore it is concluded that LEACHP has a low validation status in the context of our study.

Six tests of GLEAMS were found. Two were was sound and the remaining four were not sound. One sound test was moderately relevant and the other sound test was not relevant. In the sound and moderately relevant test the concentration level was in the range 10-100 μg dm^{-3}. The depth of the peak concentration was overestimated and the height of the peak concentration was underestimated. Both the calculated depth and height differed more than a factor of two from the measured values. The conditions in this test were suitable for GLEAMS simulations, because the model focuses on processes in the root zone and because the pesticides were retained in the top 15 cm of the profile. Therefore the poor model performance in this test is remarkable. Based on these results it is concluded that the validation status of GLEAMS is low in the context of our study.

One test of PELMO was found which was not sound. Moreover, the concentration level was in the order of 100 μg dm^{-3}. Therefore the validation status of PELMO is considered to be very low in the context of our study.

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1 Introduction

PESTLA is a simulation model to assess the potential of pesticides to leach to groundwater and to be persistent in the plough layer (Boesten and Van der Linden, 1991). It has been used since 1989 in the Dutch pesticide registration procedure as one of the tools to assess pesticide leaching to groundwater. The Dutch Long-term Crop Protection Plan (Ministerie LNV, 1991, p.87) states that PESTLA be validated before 1994. The project 'Validation of PESTLA' was initiated to assess and enlarge the validation status of PESTLA. This study was part of this project.

Boekhold et al. (1993a) described a number of definitions to be used in the project 'Validation of PESTLA'. However, for the purpose of this study we need to add the following definitions:
validation status is defined as the extent to which a model has been successfully validated within its range of validity;
range of validity is defined as that part of reality to which the validation of a model applies;
test domain is defined as that part of reality that is considered in a test of the model.

The aim of this study is to assess the validation status of other pesticide leaching models. If another model would have a much higher validation status than PESTLA, it could be appropriate to use this model instead of PESTLA. If the concepts in a model with a higher validation status would be practically identical to those in PESTLA, this would enlarge the validation status of PESTLA itself.

If a model is tested against results of field experiments, not only the computer model itself is tested: the method used for estimating input parameters is included. Moreover, it is important that this method is consistent with the intended use of the model. The approach in the Dutch Long-term Crop Protection Plan implies that the model considered should predict pesticide concentrations in groundwater on the basis of laboratory data on sorption and transformation. When testing a model for this intended use, it is not acceptable to use field-calibrated values of the sorption and transformation parameters. Therefore we will pay special attention to the procedure used to estimate parameters in the model tests.

Firstly, the concepts used in existing pesticide leaching models are briefly reviewed. Based on this review four models (PRZM-1, LEACHP, GLEAMS and PELMO) are selected for further study. Published tests of these models are reviewed. The usefulness of the test and its relevance to Dutch conditions are determined, using predefined criteria. If the test is sound and relevant the abilities of the model to simulate reality are assessed. After considering all tests the validation status of a model is determined.

Chapter 2 describes the method used in this study. In chapter 3 the characteristics of six widely used models are briefly described and four models are selected for assessment of their validation status. Each of the following chapters 4 to 7 deals with one model. These chapters are divided into four sections. The first section

describes the background of the model. The second section describes the concepts in the model and the third section gives a review of the studies in which the model has been tested. In the fourth section the overall evaluation result for each model is discussed and conclusions are drawn for each model. Finally, in chapter 8, a brief general discussion is given together with the overall conclusion.

2 Method for evaluation of model tests and for assessment of validation status

Required range of validity

The approach in the Dutch Long-term Crop Protection Plan implies that the model considered should be able to accurately predict pesticide concentrations in groundwater down to a level of about 0.1 µg dm^{-3}, on the basis of laboratory data on sorption and transformation. The required range of validity is only bound by the restriction that the application of any pesticide in Dutch agriculture and horticulture is involved. So the range of substances to be considered includes about 300 parent compounds and probably a similar number of transformation products. The soils to be considered range from sand to heavy clay and also peaty soils should be included. The range of depths of the groundwater table is roughly between 0.5 and 10 m. Crop/tillage systems to be considered include e.g. potatoes, sugar beet, wheat, maize and flower bulbs. The range of weather conditions to be considered implies a range of annual rainfall roughly between 400 and 1000 mm. So the required range of validity is very wide in view of the intended use of the model as described in the Dutch Long-term Crop Protection Plan.

Method and criteria for evaluation of model tests

A standard procedure is used to review model tests. Firstly the study is described considering the following elements: (i) background of the study, (ii) test domain (soil type and pesticide), (iii) collection of input data, (iv) monitoring of concentrations, (v) calibration, (vi) indices of comparison and criteria and (vii) results and conclusions of the authors. After this description the study is evaluated as follows. Firstly the *soundness of the study* is assessed considering whether the adsorption coefficients K_{om} or K_{oc} and the half-life of the pesticide due to transformation, DT_{50}, were determined for the specific pesticide/soil combination in laboratory experiments. Secondly, the *relevance of the study* is assessed by checking whether the test domain is within the required range of validity. This means that soil type, hydrological conditions, crop/tillage system and weather should be comparable to those in the Netherlands and that the system tested includes all important processes (e.g. a test performed on bare soil does not include plant growth and is therefore less relevant; similarly a study in which only pesticide behaviour in the top 30 cm is studied is less relevant because we are interested in leaching of low concentrations to groundwater). So relevance includes both the check whether the test domain is within the required range of validity and whether the most important processes were included in the test. Thirdly, the range of the *concentration level* of the pesticide in the soil solution at which the test took place is estimated. Because the range of validity implies that prediction of concentrations of 0.1 µg dm^{-3} in the upper groundwater should be accurate, it seems necessary that the concentration in the liquid phase deeper in the soil profile is below 5 µg dm^{-3} for a test to be relevant. In view of the importance of this aspect we consider the concentration level separately from the relevance aspect.

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The need for site-specific K_{om} and DT_{50} (which was introduced via the definition of soundness) is justified as follows. Reliable model input is essential to accurately simulate pesticide behaviour in soils. This is particularly true for input parameters to which the model output is sensitive. Boesten and Van der Linden (1991) found that PESTLA is very sensitive to both K_{om} and DT_{50} at low leaching levels: changing K_{om} or DT_{50} by a factor 2 changes the concentration in groundwater typically by about a factor of 10. Models with similar concepts for sorption and transformation processes have a similar sensitivity to these parameters (Beusen et al., 1995). K_{om} and DT_{50} may differ considerably between soil types. This means that studies without site-specific measurements of K_{om} and DT_{50} are of little value for testing a model. The outcome of the test then may be influenced to a large extent by the accidental choice of these parameters: the test may become more or less like a lottery. This is illustrated by the Figure which shows that the uncertainty in K_{om} and DT_{50} for metamitron and simazine results in an enormous uncertainty in the percentage leached. Therefore we consider a test without site-specific K_{om} or DT_{50} value to be not sound in the context of the present study.

Often the DT_{50} values are directly derived from dissipation of the pesticide in the field. This means an indirect use of measured values to reproduce these values by simulation. In this way the calculated total amount in the soil profile is fitted to the measured total amount. If DT_{50} values are obtained and used this way, the calculated residual mass and the height of peak concentrations are of little value. In these cases the study is considered to be not sound because this way of estimating this parameter does not comply with the intended use of the model.

If a study is classified as sound, a simple evaluation of *model performance* is done using the following criteria:
- calculated (peak) concentrations should be within a factor of 2 of the measured concentrations;
- calculated depth of peak concentration should be within a factor of 2 of the measured depth of peak concentration.

Thus model performance in different studies and in different situations can be roughly compared. The factor-of-f approach, which was used by Boekhold et al. (1993a) and applied to other model tests carried out in the framework of this project, will not be applied here.

When evaluating the model tests we will use qualifications for soundness, relevance and performance specified as follows.

Soundness:

sound:	both K_{om} and DT_{50} used are site-specific;
moderately sound:	one of these two parameters is site-specific and/or other constraints;
not sound:	none of these two parameters is site-specific.

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Relevance:

relevant:	the soil, the weather and the crop do not differ substantially from situations occurring in the Netherlands and the system includes all important processes;
moderately relevant:	either the soil, the weather or the crop are not relevant to situations occurring in the Netherlands or the system does not include all important processes;
not relevant:	the soil, the weather and the crop do differ notably from situations occurring in the Netherlands or the system does not include most important processes.

Model performance:

good:	both the calculated (peak) concentration and the calculated depth of the peak concentration are within a factor of 2 of the measured values;
moderate:	one of the two criteria was met;
poor:	none of the two criteria was met.

Method and criteria for assessment of validation status

The definition of validation status implies that it reflects the probability (called P) that the model will give successful predictions within the range of validity. We propose the following nomenclature for the validation status:
low if P is below 25%
moderate if P is between 25 and 75%
high if P is above 75%.

So we need a population of model tests to estimate P. Conclusions on the validation status of each model will be drawn after considering all relevant and sound tests of the model.

Fig. The fraction of pesticide dose leached below 1 m depth as a function of the organic-matter/water distribution coefficient, K_{om}, and the half-life due to transformation. The lines are contour lines calculated with PESTLA for the Dutch standard scenario by Boesten and Van der Linden, 1991; the corresponding figures are fractions in per cent. The squares are combinations of K_{om} and half-life measured for metamitron by Allen and Walker (1987); the asterisks are combinations measured for simazine by Walker and Thompson (1977); the half-lives for simazine were multiplied by 1.5 to correct for the incubation temperature of $25^{\circ}C$.

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3 Review of existing models and selection

3.1 Model classification criteria

In several reviews of modelling approaches (e.g. Addiscott and Wagenet, 1985) distinction is made between deterministic and stochastic models, between mechanistic and functional models and between rate and capacity models. Deterministic models presume that a system operates such, that the occurrence of a given set of events leads to a uniquely defined outcome, whereas stochastic models assume the outcome to be uncertain so they are structured to account for these uncertainty. Mechanistic models incorporate the most fundamental mechanisms of the processes (as much as possible), whereas the term functional is used for models that incorporate simplified treatments of water flow and solute transport. Rate models describe water flow based on Darcy's law, whereas capacity models define changes in water content by using capacity factors for water flow, such as the water contents at field capacity and wilting point.

Another possible distinction is based on the intended use of the models. Research-orientated models are developed to aid the testing of hypotheses; management-orientated models are used by decision-makers as a tool for management of agricultural resources. Research models are mostly complicated mechanistic models with a Darcian approach for water flow, whereas the less demanding (in terms of input and execution) functional models with a capacity approach serve as management models.

We will classify the models using the above characteristics. We will also consider briefly the most important processes included in the models.

3.2 Characteristics of selected pesticide leaching models

The following models are selected for this brief review:
1 PRZM-1 (Pesticide Root Zone Model - 1) was developed to evaluate pesticides leaching threats to groundwater for different crops under varying conditions; the model is widely used by the US-EPA and other users to predict chemical concentration profiles throughout and below the root zone (Carsel et al., 1985);
2 CALF (CALculates Flow) (Walker, 1987) is a combination of a model designed to simulate solute flow in structured soil (Addiscott, 1977) and a model for herbicide persistence (Walker and Barnes, 1981);
3 PELMO (PEsticide Leaching MOdel) was developed in Germany and was based on PRZM-1, but the concepts for transformation and sorption were modified (Klein, 1993);
4 GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) is a management-orientated model to evaluate the effects of agricultural management systems (Leonard et al., 1987);
5 LEACHP (Leaching Estimation And CHemistry - Pesticide) is a research-

orientated model, developed by Hutson and Wagenet (1992);

6 MACRO is a deterministic model of non-steady water flow and solute transport in a macroporous soil which allows assessment of the role of macropores on transport in field soils (Jarvis, 1991).

Table 1 lists the most important characteristics of these models. In this table the characteristics of PESTLA (Version 2.3) are included as well as a reference.

3.3 Selection of models for assessment of the validation status

The following review of the validation status is restricted to PRZM-1, GLEAMS, PELMO and LEACHP. CALF was not taken into account because a realistic simulation of the water balance of a cropped soil is not possible with this model: it does not include water uptake by plants. MACRO was not included because only one model test was available when this study was conducted. This was also the case for PELMO which was nevertheless included because it is already being used for registration purposes in Germany.

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Table 1 Main characteristics of seven models for pesticide leaching

Model	PRZM	CALF	PELMO	GLEAMS	LEACHP	MACRO	PESTLA
Version	1		1.5		3		2.3
Classification							
mechanistic (mech) / functional (funct)	funct	funct	funct	funct	mech	mech	mech
management (man) / research orientated (res)	man	res	man	man	res	res	res
Water Flow							
Darcy / capacity-approach (cap)	cap	cap	cap	cap	darcy	darcy	darcy
soil physical properties function of depth (layered soil)?	layered		layered	layered	layered	layered	layered
upper boundary condition							
partitioning (part) evaporation / transpiration?	part		part	part	part	part	part
reduction (red) of evapor. due to drying of the soil?	red	red	red	red	red	red	red
run off (ro) / erosion (ero)	ro, ero		ro, ero	ro, ero			
other bottom boundary condition possible except free drainage? (y/n)	n	[1]	n	y	y	n	y
simulation of a stagnant (stag) phase possible?						stag	
water uptake by plants included (y/n)	y	n	y	y	y	y	y
Pesticide Behaviour							
pest. behav. on plant surface simulated? (y/n)	y	n	y	y	n	y	n
convection-diffusion (cd) / mixed cell (mc)	cd	mc	cd	mc	cd	cd	cd
preferential flow (preff) simulated		preff				preff	
volatilization (volat) simulated?			volat		volat		
transformation of the pesticide							
order	1st	1st	optional	1st	1st	1st	1st
distinction of solid (s) and liquid (l) phase? (lumped = lumped rate constant for both phases)	lumped	lumped	lumped	lumped	lumped	s+l	lumped
temperature (temp) dependent?		temp	temp		temp	temp	temp
soil moisture (sm) dependent?		sm	sm		sm	sm	sm
depth dependent?	depth		depth				depth
adsorption							
freundlich (f) / linear (l)	linear	linear	freundlich	linear	freundlich	linear	freundlich
long term (lt) sorption?		lt	lt				
depth dependent?	depth		depth	depth	depth		depth
plant uptake							
proportional to water uptake (pwu)	pwu		pwu	pwu	pwu	pwu	pwu
transformation products (trf.prod)				trf.prod	trf.prod		

[1] the bottom boundary condition reflects a lysimeter-situation: upward flow of water through the bottom of the profile is not possible.

4 The Pesticide Root Zone Model - 1 (PRZM-1)

4.1 Background

The Pesticide Root Zone Model (PRZM-1) was developed by the Environmental Research Laboratory of the United States-Environmental Protection Agency (US-EPA) in Athens, Georgia. The model was developed to evaluate the risk of pesticide leaching to groundwater for different crops under divergent climatic conditions, soil characteristics and cropping practices. Its major intention is to provide a tool for environmental decision-makers. Recently, a new version (PRZM-2) has become available. We consider only the first version (PRZM-1), because we could only find tests for this version.

Carsel et al. (1984) described the background of the development of PRZM-1 as follows: 'Evaluation models should conform to the maximum possible extent to known theory but must be structured to enable efficient analysis of field situations with minimal requirements for specialized field data. The goal is to integrate the essential chemical-specific processes for leaching with reasonable estimates of water movement through soil systems. Data input requirements are to be reasonable in spatial and temporal requirements and generally available from existing data bases'. The model is intended to develop technical evaluations that can provide (Carsel et al., 1984):

— leaching potential, e.g. for new chemicals;
— frequency distributions of leaching potential that may be used in risk assessment;
— information for selecting alternative land management practices to reduce leaching.

4.2 Description of the conceptual model

Water Flow

The total evapotranspiration and water infiltration are calculated by using a simple capacity model, based on two soil moisture holding characteristics: field capacity and wilting point. The main items of the water balance equation are run-off, evapotranspiration and infiltration.

Run-off is calculated by a modification of the USA Soil Conservation Service 'curve number approach'. In this approach run-off is calculated as a function of soil type, soil drainage properties, slope, crop type and management practices (Haith and Loehr, 1979). The sum of rainfall and snow melt is partitioned in a canopy intercepted component, a run-off component and an infiltration component.

Evapotranspiration is calculated from pan-evaporation. The actual evapotranspiration is reduced if soil water is not sufficient to meet the demand. The reduction takes place before dividing the demand into soil evaporation and plant transpiration. So soil evaporation and plant transpiration are reduced following the same concept. The demand of evaporation is extracted sequentially from crop canopy storage and from

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soil moisture content of the layers within the user-defined depth of evaporation, until wilting point is reached or total demand is met. The transpiration demand is extracted sequentially from the layers of the root zone, until wilting point is reached or total demand is met.

For the calculation of the infiltration rate from a layer into a lower layer two options can be chosen (Carsel et al., 1985). Using option 1 (free drainage) the infiltration rate is calculated from the actual soil moisture content, the infiltration into this layer and the soil moisture content at field capacity. If the calculated soil moisture content is higher than field capacity, the excess of water drains to the next layer. It is assumed that water redistribution takes place within one day. Using option 2 a layered soil is considered in which permeability varies with depth. Conditions may prevail that raise the soil moisture levels in a layer above field capacity for periods of time, because water flow stagnates above a relatively impermeable layer. To accommodate these conditions two adaptations have to be made. Firstly, the assumed drainage of each layer to field capacity within a period of one day period is substituted by a kinetic drainage rule with a specific drainage rate parameter for each layer. Relatively impermeable layers drain their access of soil moisture over periods of more than one day. This means that at the end of the time step (one day) soil moisture content in these layers may exceed field capacity. Secondly a soil moisture content in access of storage capability may occur in a low permeable layer underlying a fast draining high permeable layer. To account for this, at the end of each day the profile is searched for this situation. Soil moisture in access of storage capability is redistributed into overlying layers as if the percolation of additional water beyond that necessary to saturate the low permeable layer had not occurred.

One consequence of the assumed 'drainage rules' is that the soil layers below the root zone quickly reach field capacity and remain at that value. When this condition is reached, all water percolated below the root zone will displace the water in the lower soil layer and so on. There is no allowance for lateral water movement. Water balance accounting in this manner should be most accurate for sandy soils and least accurate for clay soils.

Pesticide Behaviour

Pesticide transport by advection takes place in the aqueous phase. Dispersion and diffusion are combined, using Fick's law and assuming a combined constant coefficient. Transformation in soil is described by first-order kinetics. Transformation of adsorbed pesticide as well as pesticide in solution is taken into account. The lumped rate constant for the solid and liquid phases is assumed to be constant with temperature and moisture content, but variable with depth. Adsorption and desorption of the pesticide is simplified by assuming these processes instantaneous and reversible. A linear sorption isotherm is assumed. For each soil horizon a sorption coefficient has to be specified. If the sorption coefficient is not available, the model can estimate it from water solubility. Plant uptake of pesticide is proportional to the transpiration rate using an uptake efficiency factor. Loss by run-off is calculated as the pesticide removed from the soil system via the liquid phase of the run-off. Loss by erosion is calculated as the pesticide removed from the soil system while adsorbed

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to suspended soil particles in the run-off. The pesticide applied to the field may be intercepted by the canopy. The amount intercepted is proportional to the so-called herbage areal density. The intercepted pesticide is subject to volatilization, foliar transformation and foliar wash-off. Transformation and wash-off are combined into a first-order 'dissipation' process, with a lumped rate constant for both processes.

4.3 Review of reported studies

PAPER 1: THE PESTICIDE ROOT ZONE MODEL (PRZM): A PROCEDURE FOR EVALUATING PESTICIDE LEACHING THREATS TO GROUNDWATER (CARSEL ET AL., 1985).

Description

Background: After the development of PRZM-1 a first evaluation of model performance was carried out, using data from a study of aldicarb movement in soil. The authors did not consider this test to be a rigorous test of model performance, because no hydrological data of the site were available. The study gives a first impression of model performance only.

Test domain: Movement of aldicarb and its transformation products was followed in a loamy sand. No information is available on the crop grown during the experiment. The field site is situated in New York state with weather conditions roughly comparable to those in the Netherlands.

Collection of input: No site-specific data on soil organic matter content, soil texture and hydrological data were used for the simulations. Aldicarb and its sulfoxide and sulfone were modelled as a total toxic residue. Literature-based values for the distribution coefficient (K_{oc}) and half-life (DT_{50}) were used.

Monitoring: About one year after application of the pesticide, two soil columns were taken and analyzed to a depth of 2.5 m for total toxic residue (aldicarb + sulfone + sulfoxide).

Calibration: After a calibration-free application of the model, calibration was done by adapting the values for K_{oc} and DT_{50}. The calibrated model parameters were all within the range of measured values reported in the literature.

Indices of comparison and criteria: The calculated concentration profile was graphically compared to an average profile, calculated from the two concentration profiles measured in the columns.

Results and conclusions of the authors: In the 'calibration-free mode' the shape of the concentration profile was simulated well but downward movement of the pesticide was overestimated. The measured depth of peak concentration was 60 cm, whereas the model calculated the peak concentration to be at a depth of 110 cm. Calibration of the model by adjusting K_{oc} and DT_{50} values, as described before, made it possible to describe the measured concentration profile accurately.

Evaluation

Soundness: As the authors already stated, this study is not a sound test for model performance. Literature-based values of K_{oc} and DT_{50} were used instead of site-specific values.

Test domain: The soil used in the experiment is a sandy loam which occurs in the Netherlands as well. No information is available on the crop grown and on the weather conditions during the experiment. This test is moderately relevant.

Concentration level: Comparison of measured and calculated concentration profiles was carried out at concentrations roughly between 10 and 100 μg dm^{-3}, which is much higher than the critical concentration level in the Dutch registration procedure.

PAPER 2. COMPARISON OF PESTICIDE ROOT ZONE MODEL PREDICTIONS WITH OBSERVED CONCENTRATIONS FOR THE TOBACCO PESTICIDE METALAXYL IN UNSATURATED ZONE SOILS (CARSEL ET AL., 1986).

Description

Background: This test was part of the development and testing program of PRZM-1 and was carried out to evaluate model performance under field conditions, to indicate the predictive capability and utility of the model as a screening tool in evaluating new or existing pesticides.

Test domain: Metalaxyl was applied to two field sites, one in Florida (sand) and one in Maryland (sandy loam).

Collection of input: The K_{om} and the soil hydraulic properties were obtained from the literature. The DT_{50} was obtained from the rate of dissipation of the pesticide in the field. Meteorological data were estimated from annual average values.

Monitoring: In Florida, soil columns of 90 cm were taken at regular intervals up to 154 days after application. In Maryland similar columns were taken up to 219 days after application.

Calibration: The pan-factor for evaporation was obtained by calibration of the model to hydrological data.

Indices of comparison and criteria: Calculated and measured pesticide concentration profiles were compared graphically. The coefficient of determination, CD, was used to compare calculated and measured concentration profiles.

Results and conclusions of the authors: Measurements showed that at the end of the experiment (154 days after application) metalaxyl had moved to a maximum depth of 0.6 m in the Florida soil, whereas the pesticide did not move below 0.15 m in the Maryland site (219 days after application). Therefore, in the Florida experiment the calculated and measured concentration profiles were compared, whereas in the Maryland experiment the calculated and measured residual mass was compared. The authors concluded that:

- although PRZM-1 greatly underestimated spreading of the front by hydrodynamic dispersion, the model effectively simulated the concentration profile of the pesticide in the Florida site (coefficients of determination ranging from 0.33 to 0.95).

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- the model calculated the total residual mass with an overall coefficient of determination of 0.75.

Evaluation

Soundness: The DT_{50} was obtained from the rate of dissipation in the field and the K_{om} was not based on site-specific data. Therefore the study is not sound.

Test domain: The soils are comparable to Dutch soils. Tobacco was grown on both sites; tobacco is not grown in the Netherlands. The annual rainfall on both experimental sites was about 1000 mm, which is high in the range to be expected in the Netherlands.

Other remark with respect to relevance: Metalaxyl did not move below 15 cm depth in the Maryland site. It is concluded that this test is not relevant.

Concentration level: Comparison of measured and calculated concentration profiles was at levels roughly between 10 and 200 μg dm^{-3}, which is much higher than the critical concentration level in the Dutch registration procedure.

PAPER 3. COMPARISON OF COMPUTER MODEL PREDICTIONS WITH UNSATURATED ZONE FIELD DATA FOR ALDICARB AND ALDOXYCARB (JONES ET AL., 1986).

Description

Background: Movement of residues simulated by PRZM-1 were compared with data from 34 plots under a wide range of conditions. The emphasis of this study was to examine the accuracy of the predictions of transport velocity. Measured and calculated maximum depth of leaching, defined as the depth below which the average concentration does not exceed 5 μg kg^{-1}, were compared.

Collection of input: Field measured values of soil characteristics, meteorological data and time of application were used as input for the simulations. Soil hydraulic properties (field capacity and wilting point) were usually obtained from reported values for the particular soil class. Occasionally these parameters were obtained from laboratory measurements. First-order transformation rate coefficients were calculated from the dissipation in the field. The K_{oc} value was derived from literature to be 32 dm^3 kg^{-1}. Crop interception, loss due to erosion and plant uptake of pesticide were set to zero, since no input data were available to calculate these items.

Calibration: No calibration was carried out.

Indices of comparison and criteria: Measured and calculated maximum depth of leaching were compared.

Results and conclusions of the authors: The simulated maximum depth of leaching generally corresponded within a factor of two with the measured data, but the model is often less accurate in predicting the concentration profiles, especially without calibration of parameters. Often the movement of pesticides is overpredicted by PRZM-1. This may have the following causes: (i) the model ignores upward movement of residues with upward movement of water resulting from soil evaporation losses; (ii) less desorption occurs than calculated due to hysteresis in the adsorption-desorption isotherm, and (iii) desorption may be slow enough to affect downward

movement during a rainfall event.

The authors concluded that PRZM-1 should be limited to assessing whether a pesticide will reach groundwater in a specific situation and how long it will take for the pesticides to reach the groundwater table, and what percentage of the applied material will enter groundwater under the specified circumstances. PRZM-1 should not be used for assessment of concentrations of pesticides as function of time and depth.

Evaluation

Soundness: Using DT_{50} values, derived from the decline of total residue in the field studies is a way of curve-fitting, regulating the height of peak and the residual mass in the profile. In such cases no conclusions can be drawn from comparison of calculated and measured residual mass. Because the authors were only interested in the 'maximum' depth of leaching, and they also used this quantity for model performance assessment, this is not the major restriction of this study. The use of a single K_{oc} value for different field sites, with divergent soil physical conditions, is a rough approximation. Bromilow et al. (1980) reported K_{oc} values for aldicarb ranging between 3 and 5 dm^3 kg^{-1} for different soil types, which is much lower than the K_{oc} value of 32 dm^3 kg^{-1} used in this study. If the authors would have used a K_{oc} value of for instance 3 dm^3 kg^{-1} the calculated depth of penetration would have been considerably deeper. As no site-specific independent input data were used, these model tests are not sound.

Test domain: Little information is available on the crops, the soils and the climatic conditions in the field studies.

Concentration level: In most cases the measured and calculated pesticide concentrations ranged between 1 and 1000 μg dm^{-3}; so the concentration was mostly much higher than the concentration level which is critical in the Dutch registration procedure.

PAPER 4. EVALUATION OF FIVE SIMULATION MODELS FOR PREDICTING ALDICARB AND BROMIDE BEHAVIOUR UNDER FIELD CONDITIONS (PENNELL ET AL., 1990).

Description

Background: The purpose of this study was to test and compare five pesticide simulation models, namely (listed in order of increasing complexity): CMLS, MOUSE, PRZM-1, GLEAMS, and LEACHP. We only describe the test of PRZM-1. Data collected from a field study involving bromide and aldicarb were used to evaluate the models.

Test domain: The study was conducted for a deep, sandy, well-drained soil in Florida with low organic carbon content and high saturated hydraulic conductivity. During the 218-day simulation period aldicarb leached to considerable depths (> 7.9 m). The authors consider these data to be useful for a rigorous test for the models, because discrepancies between model calculations and measured data are likely to be more pronounced as the solute pulse leaches to a greater depth.

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Collection of input: Daily meteorologic data were collected during the field study. Sorption and transformation parameters were measured in soil samples taken from the experimental site at several depths both for aldicarb and its transformation products aldicarb sulfoxide and sulfone. Because PRZM-1 does not consider transformation products, aldicarb, aldicarb sulfoxide and aldicarb sulfone were treated as a single solute, referred to as Total Carbamate Residue (TCR). The K_{oc} of the TCR was assumed to be equal to that of aldicarb which ranged from 11 dm^3 kg^{-1} in the upper part of the profile to 36 dm^3 kg^{-1} at a depth of 3 m. TCR half-life ranged from 63 days in the surface layer to 128 days in the deeper layers. Soil hydraulic characteristics were obtained from a soil from a neighbouring site with expected similar characteristics.

Monitoring: Soil cores were taken to a depth of 7.9 m at several times up to 154 days after application. Concentration profiles of the parent compound aldicarb and the two transformation products aldicarb sulfoxide and sulfone were measured.

Calibration: The Soil Conservation Service curve number for calculation of run-off and erosion was obtained by calibration. The curve number was set to such a value that no run-off was calculated because no run-off was observed in the field.

Indices of comparison and criteria: Model evaluation was based on graphical methods and statistical functions, e.g the root mean square error. Comparison was made between measured and calculated values of (i) the solute centre of mass, defined as the depth above and below which 50 % of the total residual mass was located, (ii) the residual mass in the root zone, (iii) the residual mass in the soil profile and (iv) the shape of the concentration profiles.

Results and conclusions of the authors: Leaching velocity, characterized by the depth of centre of mass, was simulated reasonably well early in the simulation period (until 30 days). After 249 days depth of leaching was underestimated: depth of centre of mass was calculated to be at 3.5 m, whereas measured values showed a centre of mass at 7 m. Overestimation of actual evapotranspiration is mentioned as a possible reason for underestimation of leaching. Total residual mass in the root zone was simulated accurately, whereas the residual mass in the total soil profile was slightly overestimated. Dispersion was underestimated in the beginning of the simulation period (50 days after application); later in the simulation period (100-150 days after application) the shape of the concentration profile was simulated well.

Evaluation

Soundness: The values of DT_{50} and K_{oc}, and the soil hydraulic properties used for the simulations were site-specific. Therefore this field study provides a complete dataset. The study is a sound test for the assessment of model performance.

Model performance: Because this study is sound, the performance of the model in this test is roughly assessed using the criteria described in chapter 2 of this report. In this study, the calculated total residual mass and the centre of mass were both within a factor of two of the measured values during the whole experiment. According to this rough evaluation, model performance was good in this test.

Test domain: The crop on the field site was citrus, which was grown on a sandy soil with extremely low organic matter content and water retention. The very low water retention resulted in extremely deep infiltration of the water. The low organic matter content resulted in hardly any retardation of the pesticide. Cumulative rainfall was

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about 800 mm in the first 200 day; about 150 mm fell on one day. Therefore soil, crop and weather conditions are not comparable to those in the Netherlands.

Other remarks on relevance: Note that the authors stated that discrepancies between measurements and calculations are likely to be very pronounced in this field test, because the solute pulse leached to a depth of 7.9 m in one season so the test is a severe one for model performance. But this is only true for the part of the model that describes convection and dispersion. Moreover, sorption is very low in this soil so the sorption part of the model was only tested to a limited extent. In this field test the pesticide pulse leached quickly below 30 cm depth. The transformation of TCR was slow below 30 cm, so the transformation part of the model was not thoroughly tested. It is concluded that the test is not relevant.

Concentration level: Measured and calculated concentration profiles were compared at concentrations of 10-500 µg dm^{-3} for aldicarb and of 500-5000 µg dm^{-3} for TCR, which is high compared to the critical level in the Dutch registration procedure.

PAPER 5. COMPARISON OF THE PESTICIDE ROOT ZONE MODEL SIMULATED AND MEASURED PESTICIDE MOBILITY UNDER TWO TILLAGE SYSTEMS (SAUER ET AL., 1990).

Description

Background: In this study the performance of PRZM-1 was tested using a limited dataset. If no site-specific data were available, they were estimated using the techniques suggested in the PRZM manual. Off-site literature data were excluded. The authors consider this test to be a realistic test of the model's practical utility, because regulators and resource managers mostly do not have access to site-specific input parameters. A column study and a field study on the behaviour of four pesticides were used for the assessment of model performance. The two studies are described separately.

Column-study

Test domain: Carbofuran and chlorpyrifos were applied to undisturbed soil columns (length 0.9 m and diameter 0.2 m) filled with a sandy soil containing 5% organic matter in the top soil and about 2% organic matter at 1 m depth. Four columns were used (two from a no-tillage plot and two from a mouldboard-plough plot) which were exposed to natural weather conditions.

Collection of input: Soil samples were collected during excavation of the columns for determination of soil bulk density. The pesticides were applied under controlled greenhouse conditions. Corn was grown on the columns and they were irrigated. The K_{oc} was estimated from the octanol-water partition coefficient (K_{ow}) as described in the PRZM manual. The DT_{50} value was determined from the dissipation rate measured in the columns. Moisture content at field capacity was measured for this soil type by other researchers (not site-specific) and moisture content at wilting point was estimated from soil texture information. Other input parameters (such as the pan-factor for evaporation, maximum rooting depth, crop interception etc.) were not measured but were obtained from the estimation methods described in the PRZM

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manual.

Monitoring: Soil temperature, soil matric potential, drainage rate and pesticide in the leachate were monitored for 106 days. At the end of the study the columns were sectioned and organic matter and pesticide concentrations were determined for each layer. Evapotranspiration was measured by weighing the columns.

Calibration: The water flow part of the model was calibrated using the matric potentials measured in the soil profiles.

Indices of comparison and criteria: Depth of peak concentration at the end of the experiment and the cumulative amount of pesticide leached from the columns were target quantities in this experiment. The peak concentration was defined as the maximum of the concentration with depth. Model performance was considered to be acceptable if the simulated depth of pesticide penetration was within the same depth increment of 5 cm as the measured depths. The amount that was calculated to leach out of the column had to be within 20% of the measured amount.

Results: Detectable levels of carbofuran throughout the column were both measured and calculated. PRZM-1 simulated reasonably well the more or less uniform distribution of carbofuran measured throughout the column at the end of the experiment. The measured high peak concentration near the soil surface was not calculated by the model. This is explained by the authors by hysteresis in the sorption isotherms, which is not included in the model. The measured and calculated cumulative amounts of carbofuran leached from the columns showed poor agreement: the measured amounts were 3 to 10 times the calculated amounts. Chlorpyrifos did not move below 10 cm depth. The depth of the peak concentration was well simulated, whereas the residual amount in the columns was underestimated by a factor of 2 to 3.

Field study

Background: See column study.

Test domain: Atrazine and metolachlor were applied to a sandy soil with 5% organic matter in the top soil and about 2% organic matter at 1 m depth. Field plots with two tillage systems were used (mouldboard plough tillage and no tillage).

Collection of input: Soil samples were collected for determination of soil bulk density. Literature values of K_{oc} were used, whereas DT_{50} was determined from the dissipation rates in the field. Field capacity was measured for this soil by other researchers (not site-specific) and wilting point was estimated. Other input parameters were not measured but were estimated with methods described in the PRZM manual.

Monitoring: The plots were sampled immediately before and at 14, 53 and 168 days after application. Samples were taken in five increments to a depth of 1 m. Daily precipitation was measured on the site and potential evapotranspiration was obtained from a weather station.

Calibration: The water flow part of the model was calibrated to a certain extent by using the fact that no run-off occurred in the field.

Indices of comparison and criteria: The depth of peak concentration and the height of the peak concentration were used as target quantities for model performance assessment. Model performance was considered acceptable if the simulated and measured depth of peak concentration were within the same depth increment. Calculated height of peak concentration had to be within 20% of the measured

concentration.

Results: For both tillage systems and both pesticides the authors found close agreement (within one standard deviation) between the simulated and measured data after 14 days. PRZM-1 calculated deeper penetration and lower peak concentration than measured on the later sampling dates (53 and 168 days after application).

Column study and field experiment:

Conclusions of the authors: 'This study indicates that PRZM can make reasonable predictions ... under both ... tillage systems early in the growing season. ... However, the accuracy of the model predictions would likely have been improved by the increased use of site-specific input parameters, including pesticide adsorption coefficients and moisture retention characteristics ...'

Evaluation

Soundness: No site-specific K_{oc} values were used, neither in the column study nor in the field study. The DT_{50} values were simply derived from the results of the column and field experiments. So the tests with both the column and field studies are not sound.

Test domain: The soils in both the field and column experiments are comparable to Dutch soils and the crop (maize) is widely grown in the Netherlands. So the studies are relevant.

Concentration levels: Calculated and measured concentration profiles of carbofuran were compared at a concentration of the order of 10 µg dm^{-3}.

Other comments: The residual mass of chlorpyrifos was underestimated by about a factor 2 at the end of the column study. This can be explained by an overestimation of the transformation rate. However, according to the authors the DT_{50} value for chlorpyrifos was derived from the residual mass at the end of the study.

PAPER 6. FIELD TESTING AND COMPARISON OF THE PRZM AND GLEAMS MODELS (SMITH ET AL., 1991).

Description

Background: In this study results of calculations with PRZM-1 and GLEAMS were compared mutually and the calculated results were also compared to measured data. The simulations were performed in a screening mode, which means that no calibration was carried out and unknown parameters were estimated using the recommendations in the user manuals.

Test domain: In the field experiment atrazine and alachlor were applied to a sandy soil. The soil was low in organic carbon: 0.5% in the top soil and 0.05% in the layer between 1 and 2 m.

Collection of input: Literature values of K_{om} and DT_{50} were used. In previous studies soil parameters like organic matter content, dry bulk density and texture of the soil were determined. Water contents at wilting point and at field capacity and saturated

hydraulic conductivity were measured in this experiment. Daily records of precipitation, temperature and potential evapotranspiration were obtained from a nearby weather station. Crop parameters, like rooting depth, soil cover and leaf area index were estimated following the recommendations in the user manuals.

Monitoring: Up to 100 days after application concentration profiles to a depth of 2 m were measured. The soil solution was sampled at 0.6 m depth. Groundwater was sampled using a grid of piezometers and analyzed for the pesticides.

Calibration: No calibration was carried out.

Indices of comparison and criteria: Simulated peak concentrations and depth of peak concentrations were compared to measured values. For screening applications the model should be able to simulate measured concentrations within a factor of 10.

Results and conclusions of the authors: Calculated peak concentrations of atrazine were within a factor of 2 of the measured values. After about 20 days the concentration in the soil solution at 0.6 m depth reached its maximum, whereas the calculations resulted in a maximum after about 80 days. The authors attribute this to the K_{oc} value of 163 dm^3 kg^{-1} which may have been too high. At the end of the study the calculated residual mass in the soil profile was much higher than measured. This implies that the selected DT_{50} was too high.

The results for alachlor were not presented in detail. PRZM-1 calculated a far more rapid decrease in concentrations than was measured. The calculated penetration rate of alachlor was much higher than was measured. Apparently the values of K_{om} and DT_{50} were underestimated.

In all cases, the measured and predicted peak concentrations differed less than a factor 10 and in most cases they differed no more than a factor of 2 or 3. So for use in the screening mode the PRZM-1-model had met the adopted criteria for acceptance.

Evaluation

Soundness: The DT_{50} and K_{om} values were obtained from the literature for both chemicals. Therefore the test is not sound.

Test domain: The sandy soil is comparable to Dutch soils. During the experiments grass was grown, with a rooting depth of about 1 m. The pesticides were sprayed onto the grass in November. Such a pesticide application is not common in the Netherlands. So the test is moderately relevant.

Concentration level: Concentration levels ranged roughly between 10 and 300 μg dm^{-3}, which is considerably higher than the critical level in the Dutch registration procedure.

PAPER 7. TEST OF THE PESTICIDE ROOT ZONE MODEL AND THE AGGREGATE MODEL
FOR TRANSPORT AND TRANSFORMATION OF ALDICARB, METOLACHLOR, AND BROMIDE
(PARRISH ET AL., 1992).

Description

Background: The authors work at the Environmental Research Laboratory of the US-EPA in Athens, Georgia, United States. At this laboratory PRZM was developed. Model performance of the Aggregate Model is left out of consideration in this report. *Test domain:* Aldicarb and metolachlor were applied under normal agricultural practices. Application was repeated each year over a four year period (1984 to 1987). The soil is a sandy soil, with a clay subsoil at 2.5 m depth (personal communication, P.S.C. Rao, 1993). A tracer experiment with bromide ion was conducted in the same period. Bromide ion was applied once at the beginning of the first growing season. *Collection of input:* Sorption and transformation studies were carried out and sorption coefficients and half-lives were measured for each horizon (K_d for aldicarb: 0.07 to 0.04 dm^3 kg^{-1}; K_d for metolachlor: 0.72 to 0.25 dm^3 kg^{-1}; DT_{50} for aldicarb (total carbamate residue): 42 to 62 days; DT_{50} for metolachlor: 18 to 43 days). Meteorological data were obtained on a daily basis. Soil physical characteristics were measured for each of the four horizons and water contents at field capacity and wilting point were estimated.

Monitoring: Pesticide behaviour was monitored up to about 100 days after application. Bromide behaviour was monitored during the whole experimental period. Soil cores with a length of 1 to 3 m were taken.

Calibration: Estimates of the transformation rates for the upper horizon, based on dissipation in the field, tended to be significantly different from the laboratory data. For the simulations, field data for the upper horizon were used and the values for the other horizons were derived from the field data of the upper horizon and adjusted by depth in proportion to the results from the laboratory studies.

Indices of comparison and criteria: The indices for comparison were the shape of the concentration profile and the depth of peak concentration. Several statistical functions were used to assess model performance.

Results and conclusions of the authors: Metolachlor moved to a depth of about 0.35 m during the period of sampling (about 100 days after application). The shape of the concentration profiles of metolachlor and the depth of peak concentration were simulated well. PRZM-1 calculated concentrations that were within a factor of two of the measured concentrations for at least 90% of the sampling events. The total carbamate residue (TCR) resulting from aldicarb moved to a depth of 1.2 m in the same period. The shape of the concentration profiles of TCR and the depth of peak concentration were simulated less accurate than for metolachlor. The calculated concentrations of TCR were within a factor of two of the measured concentrations for about 75% of the sampling events.

As described, simulations for metolachlor were better than for TCR. The higher sorption of metolachlor results in a lower fraction in the liquid phase. Therefore errors in the transport part of the model are less significant for metolachlor than for aldicarb. The authors attribute the better results with metolachlor to a possible weakness in the hydrologic part of the model. They conclude: 'These results suggest that the

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hydrologic component of PRZM is not sufficient to simulate precisely the dynamics of chemical transport under widely varying conditions'.

Evaluation

Soundness: Because the DT_{50} value was obtained from the dissipation in the field this study is moderately sound.

Model performance: The model predicted the height and the depth of peak concentration within a factor of two of the measured value for most of the sampling events.

Test domain: The soil was a sand. Wheat was grown on the site during the experiment. Annual rainfall was about 1200 mm which is somewhat higher than normal in the Netherlands. The test is considered to be relevant.

Concentration level: The concentrations were expressed in kg ha^{-1}; measured and calculated profiles were compared at a level in the order of magnitude of 0.1 kg ha^{-1}. Taking into account the measured K_d values and the layer thickness, this areic mass corresponds to a concentration in the liquid phase of about 200 μg dm^{-3} for aldicarb and about 20 μg dm^{-3} for metolachlor. These values are 10-100 times the critical level in the Dutch registration procedure.

PAPER 8. COMPARISON OF PRZM AND GLEAMS COMPUTER MODEL PREDICTIONS WITH FIELD DATA FOR ALACHLOR, METRIBUZIN AND NORFLURAZON LEACHING (MUELLER ET AL., 1992).

Description

Background: In this test the ability of PRZM-1 and GLEAMS to simulate the movement of three herbicides was evaluated. The study aims at comparison of computed and field data, generated with measured, site-specific input data. Two field studies were used to provide site-specific input data for the models. Model performance of GLEAMS is treated in chapter 6.

Test domain: Two field studies were carried out. In the first norflurazon was applied to a loamy sand (organic matter content of 0.1-0.5 %). Management practices were typical for cotton production. In the second study alachlor and metribuzin were applied to a sandy loam, with an organic matter content between 0.1 and 0.6 %.

Collection of input: For the three pesticides, literature-based K_{om} values were used; K_{om} values taken for norflurazon, alachlor and metribuzin were 248, 190 and 95 dm^3 kg^{-1}, respectively. The DT_{50} for norflurazon was estimated from the dissipation of the pesticide in the field (DT_{50} = 69 days). For alachlor and metribuzin DT_{50} values were measured in laboratory experiments for each horizon (14-58 days and 19-43 days respectively). Meteorological data were measured on a daily basis.

Monitoring: Movement of norflurazon in loamy sand was monitored on a regular basis in a period of 89 days. Samples were taken to a depth of 60 cm. Mobility of alachlor and metribuzin in sandy loam was followed for two years under normal agricultural conditions with annual application of the herbicides. Soil samples were taken to a depth of 60 cm at regular intervals during the first 40 days after

application, which was repeated each year.

Calibration: No calibration was carried out.

Indices of comparison and criteria: For comparison of field data and simulations residual mass and maximum depth of leaching (defined as the depth below which no pesticide was detected) were used. If the calculated value was within a factor of two of the measured one, the model was considered to be accurate with regard to that target quantity.

Results and conclusions of the authors: Most of the norflurazon did not move below the top 15 cm of the profile. PRZM-1 accurately predicted the total residual mass and depth of the concentration profile of norflurazon after 84 days. Alachlor and metribuzin moved to 60 cm depth during the growing season; the simulations showed more movement of alachlor and metribuzin. The model also overestimated the residual mass after 60 days for both herbicides, but the calculated values were within a factor of two of the measured values.

The author's hypothesis for the cause of the discrepancies is that the model overestimates pesticide movement because of insufficient accuracy of input data or because of underestimation of sorption due to ignoring sorption hysteresis. This overestimation of movement may also be the cause of the overestimation of residual mass because the chemical penetrates deeper into the soil: the transformation rate decreases with depth in the model.

Evaluation

Soundness: For the simulation of norflurazon behaviour the DT_{50} value was obtained from the dissipation in the field; the K_{om} value was obtained from the literature. Therefore the norflurazon study is not sound. For simulation of metribuzin and alachlor behaviour the DT_{50} values were determined in the laboratory in soil samples from the experimental site. In this case the K_{om} values were taken from literature. Therefore this field study is considered to be moderately sound.

Model performance: Because the DT_{50} value was obtained from the measured dissipation of the pesticide in the field, the height of the peak concentration is not a meaningful criterion for assessment of model performance. Movement of both alachlor and metribuzin was overestimated by PRZM-1, but predicted depth of peak concentration was within a factor of 2 of the measured values during the experimental period of 40 days.

Test domain: The soils used in both experiments are comparable to Dutch soils. Cotton is not grown in the Netherlands. The test is therefore moderately relevant.

Concentration level: The order of magnitude of the concentrations of alachlor and metribuzin is 100 $\mu g\ dm^{-3}$, which is much higher than the critical concentration level in the Dutch registration procedure.

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PAPER 9. APPLICATION OF SIMULATION MODELS FOR THE LEACHING BEHAVIOUR OF PESTICIDES IN SOILS (VON DIBBERN AND PESTEMER, 1992).

Description

Background: Six models (including PRZM-1) were tested against results of a field study. The aims associated with the models ranged from research-oriented to management-oriented.

Test domain: The herbicide terbuthylazine was applied in September to a bare loess soil in Germany with an organic carbon content of 1.3%.

Collection of input: The K_d and DT_{50} values for terbuthylazine in this particular soil were determined in the laboratory. The DT_{50} was determined at two moisture contents and at 10 and 20 °C. Meteorological data were obtained from a meteorological station at the experimental site. Soil parameters were measured for samples taken from the site.

Monitoring: Soil samples up to 30 cm depth were taken at 22, 55, 134, 221 days after application. At 360 days after application a sample was also taken from the layer 40-60 cm.

Calibration: No calibration was carried out.

Indices of comparison: Simulated peak concentration and depth of the peak concentration (defined as the maximum of concentration with depth) were compared to measured values.

Results: After 221 days the model calculated the depth of the peak concentration to be at 10 cm depth, whereas the measured concentration profile showed that the peak concentration was still in the top 3 cm. The calculated peak concentration was within a factor of 2 of the measured peak concentration.

Evaluation

Soundness: The K_{om} and DT_{50} used for the simulations are site specific. Therefore this test is sound.

Model performance: In this study the chemical was strongly adsorbed to the solid phase. This resulted in a peak concentration in the top 3 cm of the profile after 221 days. PRZM-1 calculated the depth of the peak concentration to be at 10 cm after 221 days, which is not within a factor of 2 of the measured value. Apparently the model underestimated sorption of terbuthylazine. The height of the peak was simulated adequately; the calculated peak concentration was within a factor of 2 of the measured value.

Test domain: The sandy soil used in this experiment and the weather conditions do occur in the Netherlands.

Other remarks on relevance: The experiment was carried out with a bare soil, so the simulation of the influence of plant growth on the water flow was not tested. Moreover, terbuthylazine did not move below the top 30 cm and therefore the capability of the model to predict leaching to groundwater was not tested. It is concluded that the test is moderately relevant.

Concentration level: Measured and calculated concentration profiles were compared at concentrations in the order of 10 to 100 µg dm^{-3}, which is much higher than the concentration level of interest in the Dutch registration procedure.

4.4 Discussion and conclusion

Following the criteria for a sound test, as defined in chapter 2 of this report, only two out of the nine studies could be evaluated as sound (see Table 2). Most tests did not include site-specific K_{om} or K_{oc} and DT_{50}. The studies 7 and 8 used site-specific values for K_{oc}, but the DT_{50} values were obtained from the dissipation in the field. Of the four moderately sound and sound tests one was not relevant. As shown by Table 2 the concentration level in the tests was usually much higher than the critical level in the Dutch registration procedure (0.1 μg dm^{-3}).

Table 2 Summary of the evaluation of the tests of PRZM-1. Soundness: + = sound: +/- = moderately sound; - = not sound. Relevance: + = relevant; +/- = moderately relevant; - = not relevant. Model performance: + = good; +/- = moderate; - = poor (assessed for sound studies only). See chapter 2 for the criteria.

Criterion	Study 1	2	3	4	5	6	7	8	9
soundness	-	-	-	+	-	-	+/-	+/-	+
relevance	+/-	-	?	-	+	+/-	+	+/-	+/-
concentration level (μg dm^{-3})	10-100	10-200	1-1000	10-5000	10	10-300	20-200	100	10-100
performance				+			+	+/-	+

As shown by Table 2 model performance in the selected tests was moderate to good. In all cases the depth of the peak concentration was overestimated by PRZM-1. The extent of overestimation depended on the penetration depth of the pesticide. In cases of deep penetration of the pesticide (e.g. study 4) the overestimation was more distinct than in cases with shallow penetration, but in all cases the calculated value was within a factor of two of the measured value. Less information is available on the capability of the model to predict the dissipation in the field. Only one of the moderately sound studies (no. 8) compared the calculated and measured residual mass in the profile. In that case the residual mass was overpredicted, but was within a factor of two of the measured value. The height of peak concentration was always calculated within a factor of two of the measured value.

Broerse (personal communication, 1993) reviewed recent tests of PRZM-1 by Businelli et al. (1993), Capri et al. (1993) and Flori et al. (1993) following the same procedure as in this report. He concluded that they were not sound or not relevant.

In the three sound and relevant tests (Table 2) the concentration levels were relatively high and therefore no information is available on the capability of the model to predict concentrations at the critical level between 0.1 and 5 μg dm^{-3}. Based on these results it is concluded that the validation status of PRZM-1 is very low in the context of this study.

5 Leaching Estimation and Chemistry - Pesticide (LEACHP)

5.1 Background

LEACHP, developed at the department of Soil, Crop and Atmospheric Sciences of the Cornell University in Ithaca (New York) is a research orientated model for the fate of pesticides in the vadose zone. LEACHP is part of a group of five related models referred to as LEACHM. These five models describe the water regime and the chemistry and transport of solutes in unsaturated or partially saturated soils to a depth of about 2 m. They differ in that LEACHN describes nitrogen transport and transformation, LEACHC describes transient movement of inorganic ions, LEACHB describes microbial population dynamics, LEACHW describes the water regime only and LEACHP describes pesticide displacement and transformation. In the literature the older versions of LEACHP are often referred to as LEACHMP. In this review the LEACHP version 3, released in 1992, is described (Hutson and Wagenet, 1992).

5.2 Description of the conceptual model

Water flow

No estimations on surface processes such as run-off and erosion are included in the model. Daily potential evapotranspiration is calculated from pan evaporation and a pan factor. Daily potential transpiration is calculated from daily potential evapotranspiration and a soil cover fraction. Potential evaporation is calculated as the difference between potential evapotranspiration and transpiration. Water flow through the vadose zone is calculated using algorithms derived from Darcy's law and the equation of continuity, which are solved using a finite difference method. The upper boundary condition can be changed in time to simulate ponded or non-ponded infiltration, evaporation, or zero flux. Several bottom boundary conditions are possible, like a permanent water table, free drainage, zero flux and drainage from a lysimeter. Equations relating water content, water potential, and hydraulic conductivity are required. An adapted version of the retentivity and conductivity equations proposed by Campbell as described by Hutson (1983) are used. The constants describing the functions are needed as input. These water retention parameters may also be obtained by fitting the retention function through a measured retention curve. Besides, the model provides a choice of models for predicting water retention parameters from particle size distribution, soil bulk density and organic matter content.

Pesticide behaviour

The movement of pesticides is calculated by the convection/dispersion equation. Convection in liquid phase and diffusion in both liquid and gas phase are considered. Numerical dispersion is suppressed by using second-order approximations of the derivatives in the convection/dispersion equation. Sorption is described with the Freundlich isotherm. Moreover two-site sorption is included in the model as an option, in which a fraction f of the sites is continuously in equilibrium and a fraction 1-f is subject to kinetically controlled adsorption and desorption. For both classes of site linear sorption isotherms are assumed. The partitioning between solution and gas phase is represented by a modification of Henry's law. Diffusion in the gas phase is described by Fick's law. The effect of convection in the gas phase on the mobility of volatile chemicals in is simulated by increasing the gas diffusion coefficient. First-order microbial transformation is assumed. The behaviour of transformation products is included in the model. The transformation rate for each component is a function of moisture content and temperature. The temperature is calculated as a function of depth, time and air temperature at the soil surface by a heat flow subroutine. Plant uptake of pesticide is modelled by assuming that this process is proportional to the transpiration rate by using an uptake efficiency factor. Interception by the plant canopy and processes on the plant surface are not included in the model.

5.3 Evaluation of reported studies

PAPER 1. PREDICTING THE FATE OF NONVOLATILE PESTICIDES IN THE UNSATURATED ZONE (WAGENET AND HUTSON, 1986).

Description

Background: In this study by the developers of the model, simulations were made with the first release: LEACHMP. The main differences with LEACHP (the latest release) concern the description of sorption and the behaviour of volatile chemicals. In LEACHMP sorption kinetics were not included; sorption was described as a linear, instantaneous process. Besides, the description of the behaviour of volatile chemicals was not incorporated yet.

Test domain: Aldicarb was applied to a sandy soil with less than 1% organic matter. *Collection of input:* Texture, organic matter content and pH were measured for samples from the site. The hydraulic properties of the soils were generated by methods using measured bulk density, texture and saturated conductivity values. Pan evaporation, temperature and precipitation were measured at the site. Potatoes were grown on the site during the experiment and normal growing practices were followed during the summer. Aldicarb was applied at planting. The DT_{50} values were obtained from a laboratory study of aldicarb transformation in a soil similar to the soil used in this experiment. No information is given on the source of the K_{oc} values used. *Monitoring:* Soil samples were collected at 29, 64 and 124 days after application to a depth of 1.5 m. Water and pesticide contents were measured.

Sensitivity analyses: The sensitivity of the model to the use of two different sets of

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hydraulic properties and different combinations of DT_{50} values was examined.
Indices of comparison: The shape of the concentration profile, the water content profile and the residual mass of pesticide in the profile were used as indices of comparison.

Results and conclusions of the authors: Almost no leaching occurred beyond 0.3 m depth. The model predicted water content within the range defined by the measured mean water content plus and minus one standard deviation of the mean. The pesticide contents higher than 200 µg kg^{-1} were predicted within the range defined by the measured mean plus and minus one standard deviation of the mean, whereas the pesticide contents lower than 200 µg kg^{-1} were predicted within the range defined by the mean plus and minus four times the standard deviation of the mean. All predictions were within a factor of 2 of the measured mean.

Evaluation

Soundness: The source of the K_{oc} values used for aldicarb and its transformation products is not mentioned in the paper. Because no statements are made about sorption experiments in the laboratory, it is assumed that literature values were used. Therefore the ability of the model to predict the transport of organic chemicals can not be tested. The authors concentrate on the comparison of concentration levels, which is meaningful because DT_{50} values were determined in an incubation experiment in a soil similar to the soil used in the experiment. Note that a poor simulation of the movement of the pesticide, due to errors in the K_{oc} value, influences transformation as well in situations where the transformation rate changes with depth. In view of this the soundness of this study is moderate.

Test domain: Soil, crop and weather do not differ substantially from Dutch situations.
Concentration level: At the end of the experiment (124 days after application) the concentration of TCR in soil solution was about 100 µg dm^{-3}. This is high compared to the critical concentration level in the Dutch registration procedure.

PAPER 2. EVALUATION OF FIVE SIMULATION MODELS FOR PREDICTING ALDICARB AND BROMIDE BEHAVIOUR UNDER FIELD CONDITIONS (PENNELL ET AL., 1990).

Description

For a description of the field experiment the reader is referred to section 4.3 (paper 4). In this section the results of the LEACHP simulations and the conclusions of the authors related to these simulations are given.

Results and conclusions of the authors: Leaching velocity was simulated reasonably well in first 30 days. After 249 days the depth of leaching is underestimated: depth of centre of mass was calculated to be 4.5 m whereas 7 m was measured. Overestimation of actual evapotranspiration is mentioned as a possible reason for the underestimation of leaching. Total residual mass of TCR in the root zone was simulated adequately; the total residual mass in the total profile was only slightly overestimated. Dispersion was underestimated in the beginning of the simulation

period *(50 days after application);* later *(100-150 days after application)* the shape of the concentration profile was simulated better.

Evaluation

Soundness: In section 4.3 (paper 4) it was already concluded that this study is a sound test.

Model performance: Using the criteria as defined in chapter 2, it can be stated that:
(i) LEACHP calculates the height of the peak concentration to be within a factor of 2 of the measured peak concentration
(ii) LEACHP calculates the depth of peak concentration to be within a factor of 2 of the measured depth peak concentration.

Test domain: In section 4.3 (paper 4) it was concluded that this test is not representative for any situation in Dutch agriculture. Both crop and soil deviate strongly from crops and soils occurring in the Netherlands.

Concentration level: The measured and calculated concentration levels range from 10 μg dm^{-3} for aldicarb to 5000 μg dm^{-3} for TCR, which is high compared to the critical level in the Dutch registration procedure.

PAPER 3. APPLICATION OF SIMULATION MODELS FOR THE LEACHING BEHAVIOUR OF PESTICIDES IN SOILS (VON DIBBERN AND PESTEMER, 1992).

Description

For a description and an evaluation of the field experiment the reader is referred to section 4.3 (paper 9). In this section the results of the LEACHP simulations are given.

Results: After 221 days the model calculated a depth of peak concentration at 8 cm depth, whereas the measured concentration profile showed the peak concentration to be in the top 3 cm. The calculated height of the peak concentration was about half of the measured peak concentration.

Evaluation

Soundness: In section 4.3 (paper 9) it was concluded that this study is a sound test of model performance. For both K_{om} and DT_{50} site-specific values were used.

Model performance: Using the criteria, as defined in chapter 2, it can be stated that:
(i) LEACHP calculates a height of the peak concentration that is within a factor of 2 of the measured peak concentration
(ii) the calculated depth of the peak concentration is 3 to 5 times that measured, so LEACHP does not meet this criterion.

Test domain: The soil type and weather conditions also occur in the Netherlands.

Other remarks with respect to relevance: Because this test was carried out with bare soil it is moderately relevant.

Concentration level: The level of the measured and calculated concentrations ranges

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roughly from 10 to 100 µg dm^{-3}, which is much higher than the critical level in the Dutch registration procedure.

5.4 Discussion and conclusion

As is shown by Table 3 all three test were (moderately) sound and two tests were (moderately) relevant to Dutch situations. In these three tests LEACHP overestimated the movement of the pesticides, but the calculated depth of peak concentration was always within a factor of two of the measured values. Little information is available on the capability of the model to predict the dissipation in the field. In the three tests the concentration levels were comparatively high (see Table 3) and therefore no information is available on the capability of the model to predict concentrations at the critical level (0.1 µg dm^{-3}). Based on these results it is concluded that LEACHP has a low validation status in the context of this study.

Table 3 Summary of the evaluation of the tests of LEACHP. Soundness: + = sound: +/- = moderately sound; - = not sound. Relevance: + = relevant; +/- = moderately relevant; - = not relevant. Model performance: + = good; +/- = moderate; - = poor (assessed for sound studies only). See chapter 2 for the criteria.

Criterion	Study		
	1	2	3
soundness	+/-	+	+
relevance	+	-	+/-
concentration level (µg dm^{-3})	100	10-5000	10-100
performance	+	+	+/-

6 Groundwater Loading Effects of Agricultural Management Systems (GLEAMS)

6.1 Background

GLEAMS is a mathematical model developed to evaluate at the field scale the effects of agricultural management systems on the movement of agricultural chemicals within and out of the root zone (Leonard et al., 1990). The model focuses on the root zone and the processes that are especially important for this zone (precipitation, run-off, erosion, evaporation, transpiration, effects of different tillage systems on the processes etc.). The vadose zone below the root zone is not covered by the model; leaching out of the root zone is referred to as 'groundwater load'.

The model is an extension of the extensively used CREAMS model (Knisel, 1980). The CREAMS model had the capability to simulate differences in water, sediment, and chemical responses resulting from different management practices. GLEAMS retains the ability of CREAMS to simulate sophisticated scenarios of management practices.

6.2 Description of the conceptual model

Water flow
The USDA-SCS (United States Department of Agriculture - Soil Conservation Service) curve number technique is used for predicting run-off from daily rainfall. In this approach run-off is calculated as a function of soil type, soil drainage properties, crop type and management practices (Haith and Loehr, 1979). The amount of run-off is subtracted from total precipitation. Erosion is modeled using methods developed by Foster (1980). Eroded soil is routed with run-off by particle size, which enables calculation of storm-by-storm sediment enrichment ratios for use in estimating adsorbed pesticide transport.

Soil evaporation and plant transpiration are estimated with a modified Penman equation. Potential evapotranspiration is calculated from daily mean air temperature and net solar radiation. The model divides potential evapotranspiration into potential evaporation and transpiration on the basis of the leaf area index. The actual soil evaporation is obtained by reducing the potential soil evaporation, based on moisture availability in the top soil. Soil evaporation is subtracted from the moisture content in the upper soil zone only. The demand of plant transpiration is distributed over the soil profile by a root growth simulation model in which the rate of water uptake is a function of rooting depth.

Water moves from the upper surface zone as a function of the difference in saturation between two zones, which is roughly analogous to Darcy's law. In the remainder of the soil profile infiltration is simulated by application of the capacity approach,

which means that the rate of infiltration from a layer into a lower layer is calculated from the actual soil moisture content, the infiltration into this layer and the soil moisture content at field capacity. If the calculated soil moisture content is higher than field capacity, the excess of water is allowed to drain to the lower zone. It is assumed that water redistribution takes place within one day.

Pesticide behaviour

Since the main objective of the GLEAMS model is to simulate the effects of management practices on pesticide movement within and out of the root zone, the emphasis is on superficial processes like erosion-loss, plant uptake and foliar interception. Therefore a surface control layer is defined. The concentration in this surface control layer determines the amount of pesticide that is available for surface run-off and movement into the soil. In the field the thickness of this layer varies with soil density, surface roughness, soil water content and pesticide characteristics. Good relationships to calculate the actual surface layer thickness have not been developed yet. Therefore the surface layer in GLEAMS has a constant thickness of 1 cm.

Pesticide transformation in the root zone as well as on plant foliage is described by first-order kinetics. The transformation rate is assumed to be constant in the root zone. Rate constants for foliar transformation and transformation in soil are lumped constants, accounting for total dissipation of the chemical. In a second version, released in 1990 (Leonard al., 1990), the model was modified to simulate the formation and transformation of pesticide transformation products. A linear adsorption isotherm is used. Adsorption and desorption are assumed to be instantaneous and reversible. The adsorption isotherm is also used for the calculation of the concentration of the pesticide in run-off.

Plant uptake of pesticides from the appropriate layer is assumed to be proportional to the amount extracted from the layer for transpiration. In the second version of the model (Leonard et al., 1990) an exponential function is added that relates the transpiration stream concentration factor (the parameter determining the relation between transpiration and plant uptake) to the octanol-water partitioning coefficient (K_{ow}) of the compounds. If evaporation occurs from the top layer in the model, the pesticide is not moved out of the soil, because volatilization is not modelled.

6.3 Review of reported studies

GLEAMS is an extension of the extensively tested and used model CREAMS. Since CREAMS is focusing on the root zone, studies on this model mostly test the representation of run-off, erosion and root zone processes. In the context of our project we are mainly interested in the leaching of pesticides to groundwater; therefore this review only contains tests of GLEAMS.

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PAPER 1. GLEAMS: GROUNDWATER LOADING EFFECTS OF AGRICULTURAL MANAGEMENT
SYSTEMS (LEONARD ET AL., 1987).

Description

Background: This study describes the model and four tests performed by the developers of GLEAMS. The tests were a first check of the performance of the model. Existing data sets of studies on pesticide behaviour were used.

Test domain: On two locations in Lincoln (IA), watershed ISU-1 and ISU-2, cyanazine and alachlor were applied to a silt loam soil. In Watkinsville (GA) atrazine was applied to a sandy loam. In Tifton (GA) atrazine behaviour was monitored in a sandy soil, which is very permeable, has a low organic matter content and shows low water retention. In ISU-1 the site was planted with corn, while in ISU-2 soybeans were grown. No information is available on the crops in Watkinsville and Tifton.

Collection of input: In all studies the soil parameters are site specific. In none of the studies site-specific pesticide parameters (K_{om} and DT_{50}) have been used.

Monitoring: For none of the field studies specific information on the depth of the measurements is available. The discussion indicates that in the field studies the emphasis of the measurements is on the top soil (0-50 cm). The ISU-1 and ISU-2 field studies lasted 120 days. In Watkinsville the experiment lasted only 30 days and in Tifton 40 days.

Calibration: No calibration was carried out.

Indices of comparison and criteria: No clear criteria have been defined.

Results and conclusions of the authors: In the ISU-1 and ISU-2 experiments none of the pesticides moved below the top 10 cm. In Watkinsville the pesticide leached into the 10-20 cm layer and only traces were found below this zone. In Tifton atrazine leached up to 40 cm deep and traces were found below this level. The estimated pesticide concentrations differed less than one standard deviation from the mean of the measured values in the ISU-1, ISU-2 and Tifton experiments. In the Watkinsville experiment the calculated concentrations in the profile differed more (about a factor 5-10) from those measured.

Evaluation

Soundness: In none of the studies site-specific pesticide parameters were used. So the study is not a sound test for model performance.

Test domain: The information available on the domain of the studies does not indicate an important deviation from Dutch situations. Soils were representative for the Netherlands, whereas the crops were deviating from crops grown in the Netherlands.

Other remarks with respect to relevance: The duration of the tests was short, so little or no pesticide leached below the top 20 cm in ISU-1, ISU-2 and Watkinsville. In the Tifton experiment pesticide concentrations were measured up to 40 cm depth. Therefore the capability of the model to simulate leaching to groundwater could not be tested. So the test is not relevant.

Concentration level: The concentrations in all studies range between 100 and 1000 $\mu g\ dm^{-3}$, which is far above the critical concentration level in the Dutch registration procedure.

PAPER 2. VALIDATING GLEAMS WITH FIELD DATA FOR FENAMIPHOS AND ITS METABOLITES (LEONARD ET AL., 1990).

Description

Background: This study was performed to test a modification of the model, that made it possible to simulate behaviour of pesticide transformation products.

Test domain: Fenamiphos was applied to a loamy sand in spring and in summer. Transformation of fenamiphos and formation and transformation of fenamiphos sulfoxide and fenamiphos sulfone were monitored. Sweet corn, millet and another winter cover crop were grown on the field site during the experiment.

Collection of input: In the paper no information is given on the collection of soil parameters. Pesticide parameters were obtained from the literature. After a first run the DT_{50} value for fenamiphos and its transformation products were changed to obtain a better fit of measured and predicted concentrations.

Monitoring: Field samples were taken to a depth of 30 cm in a period of four months after the first application of the pesticide. The samples were analyzed for fenamiphos and its transformation products fenamiphos sulfoxide and fenamiphos sulfone

Indices of comparison and criteria: Measured and calculated residual mass (in kg ha^{-1}) and measured and calculated concentration profiles in soil at 6 and 14 days after application were compared.

Results and conclusions of the authors: Residual mass in the top 30 cm was well simulated during the whole experimental period. The measured and calculated concentration profiles coincided within one standard deviation of the mean at 6 and 14 days after application. The authors concluded: 'GLEAMS-simulated residual mass of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone compared favourable with field data within the variability of the data. Simulated and observed concentrations with depth in the soil also closely corresponded. Results of the limited test gave confidence that the (newly implemented) model component is performing as conceptualized.'.

Evaluation

Soundness: The pesticide input data K_{om} and DT_{50} were obtained from the literature. DT_{50} values were altered after a first run to obtain a better fit. The study is therefore not sound.

Test domain: Soil and crop are representative for situations in the Netherlands.

Other remarks with respect to relevance: The nematicide and its transformation products did not move below the top 30 cm of the profile, so the capability of the model to simulate leaching could not be tested. Moreover, the comparison is made only at 6 and 14 days after application. So the test is only moderately relevant.

Concentration level: The concentrations in the studies ranged between 300 and 1000 µg dm^{-3}, which is far above the critical concentration level in the Dutch registration procedure.

PAPER 3. EVALUATION OF FIVE SIMULATION MODELS FOR PREDICTING ALDICARB AND
BROMIDE BEHAVIOUR UNDER FIELD CONDITIONS (PENNELL ET AL., 1990).

Description

For a description of the field experiment the reader is referred to section 4.3 (paper 4). In this section the results of the GLEAMS simulations and the conclusions of the authors related to these simulations are given.

Results and conclusions of the authors: The depth of centre of mass and the total residual mass in the profile are inappropriate indices of comparison for assessment of performance of the GLEAMS model because the model concentrates on root zone processes. The total residual mass in the root zone is a more appropriate target quantity. Total residual mass in the root zone was largely overestimated by GLEAMS and the same holds for the amount of aldicarb near the soil surface. The poor prediction of the concentrations in the root zone by GLEAMS is remarkable, but may be explained by the fact that the chemicals had been leached out of the root zone after day 49. The GLEAMS model appeared to have little utility for predicting pesticide fate and transport in the unsaturated zone, particularly for pesticides exhibiting low sorption and applied to soils with high saturated hydraulic conductivity.

Evaluation

Soundness: The values of DT_{50} and K_{om} and the soil hydraulic properties used for the simulations were site-specific. Therefore the study is sound.

Model performance: Model performance could not be established using the criteria in chapter 2, because calculated concentration profiles were not given in the paper.

Test domain: As described in Section 4.3 (paper 4) the test domain is not relevant.

Concentration level: Measured and calculated concentration levels range from 10 $\mu g\ dm^{-3}$ for aldicarb to 5000 $\mu g\ dm^{-3}$ for TCR, which is high compared to the critical concentration level in the Dutch registration procedure.

PAPER 4. FIELD TESTING AND COMPARISON OF THE PRZM AND GLEAMS MODELS (SMITH ET AL., 1991).

PAPER 5. COMPARISON OF PRZM AND GLEAMS COMPUTER MODEL PREDICTIONS WITH FIELD DATA FOR ALACHLOR, METRIBUZIN AND NORFLURAZON LEACHING (MUELLER ET AL., 1992).

The papers 4 and 5 were described in section 4.3. In this section it was concluded that these tests were not sound and that the test domains were not relevant to Dutch situations. These qualifications are independent of the models used for the simulations, so the description and evaluation of these tests are not repeated here; the reader is referred to section 4.3.

For a description of the field experiment the reader is referred to section 4.3 (paper 9). In this section the results of the GLEAMS simulations are discussed.

Description

Results: After 221 days the model calculated the peak concentration of terbuthylazine to be at 15 cm depth, whereas the measured concentration profile shows that the peak concentration was still in the top 3 cm. The model calculated a concentration profile that was much more dispersed than the measured profile.

Evaluation

Soundness: Soil parameters, hydraulic properties (water retention curves and unsaturated hydraulic conductivity curves) and pesticide parameters (K_{om} and DT_{50}) used for the simulations were all site specific; therefore this study is considered to be moderately sound.

Model performance: In this study the chemical was strongly adsorbed to the solid phase. This resulted in a peak concentration in the top 3 cm of the profile after 221 days. GLEAMS calculated a dispersed concentration profile with the depth of the peak concentration at 15 cm after 221 days, which is not within a factor of 2 of the measured value. The height of the peak concentration was calculated to correspond with 0.5 mg kg^{-1} whereas 2 mg kg^{-1} was measured, so the model did not calculate the peak concentration within a factor of 2 of the measured value. The poor model performance in this test is remarkable.

Test domain: The sandy soil used in this experiment and the weather conditions occur also in the Netherlands.

Other remarks with respect to relevance: The experiment was carried out with bare soil, so no crop was included. Moreover, terbuthylazine did not move below the top 30 cm of the profile and therefore the capability of the model to predict leaching is not tested. So the test is only moderately relevant.

Concentration level: The measured and calculated concentration levels were roughly between 10 and 100 µg dm^{-3}, which is higher than the critical concentration level in the Dutch registration procedure.

6.4 Discussion and conclusion

As shown in Table 4 two tests were sound and only one was moderately relevant. In this sound and moderately relevant test the model overestimated the depth of peak concentration and it underestimated the height of peak concentration. The calculated values were outside the range of a factor of two of the measured values. The poor model performance in this test is remarkable. Because the pesticide was retained in the top 15 cm of the profile, the circumstances in this test were explicitly suitable for GLEAMS simulations, because the model focuses on processes within the root

zone. It is concluded that the validation status of GLEAMS is extremely low in the context of our study.

Table 4 Summary of the evaluation of the tests of GLEAMS. Soundness: + = sound: +/- = moderately sound; - = not sound. Relevance: + = relevant; +/- = moderately relevant; - = not relevant. Model performance: + = good; +/- = moderate; - = poor (assessed for sound studies only). See chapter 2 for the criteria.

Criterion	Study 1	2	3	4	5	6
soundness	-	-	+	-	-	+
relevance	+/-	+	-	-	-	+/-
concentration level ($\mu g\ dm^{-3}$)	100-1000	300-1000	10-5000	10-300	100	10-100
performance			?			-

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7 Pesticide Leaching Model (PELMO)

7.1 Background

The PELMO model (Klein, 1993) was developed in Germany for estimating the potential of agricultural chemicals to leach to groundwater, using soil and pesticide data already available for the registration procedure in Germany. The model is based on the PRZM-1 model. This section gives a description of the concepts used in version 1.5 of the PELMO model. Because the only study found in the literature applies to version 1.1 of the model the differences between versions 1.1 and 1.5 are described as well. The description focuses on the differences between PELMO and PRZM-1; for the concepts that are similar to concepts in PRZM-1, the reader is referred to section 4.2 of this report.

7.2 Description of the conceptual model

Water Flow
The simulation of water flow is very similar to that in PRZM-1. The water balance equations are solved separately from the pesticide mass balance equation. The total evapotranspiration and infiltration are calculated by using the capacity model, based on two soil moisture holding characteristics: field capacity and wilting point. Run-off is simulated as in PRZM-1. The potential evapotranspiration can be calculated by using pan-evaporation or by using the Haude-equation (Haude, 1952). It is also possible to give the potential evapotranspiration as input. The evaporation is reduced if sufficient soil water is not available to meet the demand. The reduction takes place before the total demand is divided into soil evaporation and plant transpiration. So soil evaporation and plant transpiration are reduced following the same concept. The demand of evaporation is extracted sequentially from crop canopy storage and soil moisture content of the layers within the user-defined depth of evaporation, until the wilting point is reached or the total demand is met. Transpiration demand is extracted sequentially from the layers of the root zone, until the wilting point is reached or the total demand is met. Water infiltration and redistribution is simulated as in PRZM-1.

Pesticide Behaviour
The order of the transformation kinetics is optional. The transformation rate coefficient is calculated from the half-life and the order of reaction kinetics chosen. Transformation of adsorbed pesticide as well as pesticide in solution is taken into account. The lumped rate coefficient for the solid and liquid phases is a function of soil temperature, moisture content and depth. The soil temperature is calculated from air temperature. Instantaneous and reversible adsorption and desorption is assumed and sorption is described by the Freundlich isotherm. For each soil horizon a specific sorption coefficient can be given as input. If no partition coefficient is available, pesticide solubility can be given as input for estimation of the partition

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coefficients. In version 1.5 sorption strength can increase linearly with time; the extent of the increase can be specified. Transport in the gas phase is included in version 1.5. The partitioning between solution and gas phase is represented by a modified Henry's Law. Diffusion in the gas phase is described by Fick's law.

Dispersion, diffusion, uptake of the pesticide by plant roots, run-off-loss, erosion-loss, interception of the pesticide by the plant canopy, and the foliar behaviour of the pesticide are modeled in the same way as in PRZM-1 (see section 4.2).

7.3 Review of reported studies

PAPER: SIMULATION OF THE WATER BALANCE AND THE BEHAVIOUR OF METHABENZ-THIAZURON IN LYSIMETERS AND A FIELD TRIAL WITH TWO SIMULATION MODELS (GOTTESBÜREN ET AL., 1993)

Description
Background: This study aimed at the comparison of the simulation results of PELMO and VARLEACH, two models that are used for the simulation of pesticide behaviour in soils. In this review model performance of PELMO is considered only.
Test domain: Four data sets were used for the assessment of model performance: three lysimeter studies (with an area of 1 m^2 and a length of 1.1 m) and one field study. The lysimeters contained undisturbed soil from a silty loam, with 1.3 % organic matter in the top 40 cm and about 0.4 % lower in the profile. In the field experiment the same soil was used. In two lysimeter studies (L2 and L3) the leachate was monitored every 2 weeks. The first lysimeter study and the field study were performed only for pesticide behaviour; the second and third lysimeter study were performed for pesticide behaviour as well as the calculation of the water balance.
Collection of input: The field capacities were calculated from soil texture using pedotransfer functions. The origin of the weather data is not described but it may be expected that they were measured at the experimental field and close to the lysimeters. The K$_d$ and DT$_{50}$ values were estimated from the literature.
Monitoring: For the first lysimeter study (L1) and the field study (F1) pesticide concentrations in soil to a depth of 0.4 m were determined at 129 and 133 days after application. For the remaining lysimeter studies (L2 and L3) pesticide concentrations to a depth of 0.2 m were determined at 245 and 259 days after application. Besides this, the cumulative amount of leachate in the lysimeter studies L2 and L3 was monitored.
Calibration: No calibration was performed in this study.
Indices of comparison and criteria: Predicted pesticide concentration profiles were compared visually with measured profiles. Besides that, the residual mass of pesticide in the root zone was used for comparison of calculations and measurements.
Results and conclusions of the authors: In all studies methabenzthiazuron did not move below 10 cm depth. PELMO calculated the depth of the peak concentration within the 0-10 cm layer in all cases. The decline in residual mass in the field and lysimeter experiments was simulated reasonably well. In lysimeter L2 PELMO

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simulated cumulative water percolation well until 400 days after application. PELMO overestimated the moisture content in the top layer in a dry period in summer. In lysimeter L3 PELMO calculated the first percolation of water to occur after 50 days, whereas in reality percolation started at the first day. In this experiment the soil did not dry to the same extent as in experiment L2; the measured volume fraction of liquid was at least about 0.2. The volume fraction of liquid in the top 20 cm was simulated well by PELMO in this case.

Evaluation

Soundness: With respect to pesticide leaching this study is not sound, because a literature-based value for the DT_{50} was used. The K_d value was determined in a similar soil, but samples from another location were used.

Test domain: Soil type and crop occur also in the Netherlands.

Concentration level: The concentrations were in the order of about 1000 µg dm^{-3}, which is high compared to critical level in the Dutch registration procedure.

Other remarks: The measured volume fraction of liquid in the top 0.2 m of 0.01 in lysimeter L3 may be erratic. In view of the clay content of 15% of the top 39 cm it seems unlikely that the soil dried that drastically.

7.4 Discussion and conclusion

Following the criteria for a sound study, defined in chapter 2 of this report, the only study reported is not sound. The values of DT_{50} and K_{om} used in this study were not site-specific. Besides that, the concentration level was much higher than the critical level in the Dutch registration procedure. So the validation status of PELMO is very low in the context of our study.

8 General discussion and conclusion

From this literature study it is concluded that the validation status of all models considered is low to very low. However, it is stressed that the validation status of a model is a function of the intended use of the model and of the range of validity that is required. In this study the requirements (specified by the Long-term Crop Protection Plan of the Dutch government) were very stringent: the range of validity had to be very wide, the critical concentration level was very low and the intended use implied that calibration of pesticide/soil parameters was not acceptable. If we would have assessed the validation status at concentrations in the range 100 to 1000 $\mu g\ dm^{-3}$, the results would have been more positive. At such high leaching levels sensitivity of the models to sorption and transformation parameters is much lower than at the low leaching levels. Therefore the soundness criterion as used in the present study would not be necessary for assessment at high concentration levels. More studies would have been considered for these high levels (e.g. for PRZM-1; see Table 2).

This study considered the validation status of all models considered relevant except PESTLA. Admittedly, the validation status of PESTLA (if assessed according to the same standards as used here) is also low as follows already from the limited number of tests available (Boekhold et al., 1993b; Van den Bosch and Boesten, 1994).

The conclusions of this study might lead to the impression that models are not useful in the pesticide registration procedure and that the registration should be based on measurements only. However, we disagree strongly with the use of measurements only in pesticide registration. The procedure followed here to assess the validation status of models was very strict: we operationalized the concept of validation status by linking it to the probability of a successful model prediction. If we would apply a similarly strict approach to measurements (i.e. measurements should give a statistically reliable estimate for the required range of conditions), this would certainly lead to the requirement of enormous amounts of measurements for each pesticide in each country. Another restriction of the measurements is that conclusions can only be drawn after the pesticide has been studied for many years e.g. under a wide range of weather conditions. So the most economic and efficient way to assess pesticide leaching is to combine information from modelling studies and from experiments. This can be done via tiered approaches in evaluation schemes (e.g. using decision trees).

References

Addiscott, T.M., 1977. 'A simple computer model for leaching instructured soils'. *Journal of Soil Science* 28: 554-563.

Addiscott, T.M. and R.J. Wagenet, 1985. 'Concepts of solute leaching in soils: a review of modelling approaches'. *J. of Soil Sci.* 36, 411-424.

Allen, R. and A. Walker, 1987. 'The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin'. *Pestic. Sci.* 18, 95-111.

Beusen, A.H.W., A.E.Boekhold, A.M.A. van der Linden and G.B. Makaske, 1995. *Validation of the PESTLA model: Comparison of PRZM-1, PELMO, LEACHP and PESTLA using the standard PESTLA dataset.* RIVM report no. 715802003. National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.

Boekhold, A.E., H. van den Bosch, J.J.T.I. Boesten, M. Leistra, F.A. Swartjes and A.M.A. van der Linden, 1993a. *Validation of the PESTLA model: Definitions, objectives and procedure.* RIVM report no. 715802001. National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.

Boekhold, A.E., F.A. Swartjes, F.G.G. Hoogenboom and A.M.A. van der Linden, 1993b. *Validation of the PESTLA model: Field test using data from a sandy soil in Schaijk (the Netherlands).* RIVM report no.715802002. National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.

Boesten, J.J.T.I. and A.M.A. van der Linden, 1991. 'Modelling the influence of sorption and transformation on pesticide leaching and persistence'. *J. of Environ. Qual.* 20, 425-435.

Bosch, H. van den and J.J.T.I.Boesten, 1994. *Validation of the PESTLA model: Field test for leaching of two pesticides in a humic sandy soil in Vredepeel (The Netherlands).* Report 82, DLO Winand Staring Centre, Wageningen, the Netherlands, 59 pp.

Bromilow, R.H., R.J. Baker, M.A.H. Freeman and K. Gorog, 1980. 'The degradation of aldicarb and oxamyl in soil'. *Pest. Sci.* 11, 371-378.

Businelli, M. C.Vischetti and M. Marini, 1993. *Validation of the PRZM model in two field trials cropped with maize and tobacco.* In: Proceedings IX Symposium Pesticide Chemistry, A.A.M. Del Re, E. Capri, S.P. Evans, P. Natali and M. Trevisan (Eds), Istituto di Chimica Agraria ed Ambientale, Piacenza, Italy, p. 63-72.

Capri, E., M. Trevisan and A.A.M. Del Re, 1993. *Herbicide residues under different soil management. II. The model simulation.* In: Proceedings IX Symposium Pesticide Chemistry, A.A.M. Del Re, E. Capri, S.P. Evans, P. Natali and M. Trevisan (Eds), Istituto di Chimica Agraria ed Ambientale, Piacenza, Italy, p. 73-84.

Carsel, R.F, C.N. Smith, L.A. Mulkey, J.D. Dean and P. Jowise, 1984. *Users manual for the Pesticide Root Zone Model (PRZM).* Environmental research laboratory, US Environmental Protection Agency, EPA-600/3-84-109.

Carsel, R.F., L.A. Mulkey, M.N. Lorber and L.B. Baskin, 1985. 'The pesticide root zone model (przm): a procedure for evaluating pesticide leaching threats to groundwater'. *Ecolog. Modelling.* 30, 49-69.

Carsel, R.F., W.B. Nixon and L.G. Ballantine, 1986. Comparison of pesticide root zone model predictions with observed concentrations for the tobacco pesticide metalaxyl in unsaturated zone soils. *Environ. Tox. Chem.* 5, 345-353.

Dibbern, H. von and W. Pestemer, 1992. 'Anwendbarkeit von Simulationsmodellen zum Einwaschungsverhalten von Pflanzenschutzmitteln im Boden'. *Nachrichtenbl. Deut. Pflanzenschutzd.* 44, 134-143.

Flori, P., A. Rambaldi, P. Sgarbi and G. Malucelli, 1993. *Herbicide mobility and persistence in soil: comparison between experimental data and predictions by means of the pesticide root zone model (PRZM) for the validation of mathematical model.* In: Proceedings IX Symposium Pesticide Chemistry, A.A.M. Del Re, E. Capri, S.P. Evans, P. Natali and M. Trevisan (Eds), Istituto di Chimica Agraria ed Ambientale, Piacenza, Italy, p. 105-115.

Foster, G.R., 1980. *A model to estimate sediment yield from field-size areas: Development of model. CREAMS: A field-scale model for chemicals, run-off, and erosion from agricultural management systems* (Conservation Res. Report No. 26), W.G.Knisel (ed.), U.S. Dept. Agr., Science and Education Administration, 36-64.

Gottesbueren, B., H. Printz, T. Puetz, W. Mittelstaedt & F. Fuehr, 1993. *Simulation of the water balance and the behaviour of methabenzthiazuron in lysimeters and a field trial with two simulation models.* Proceedings IX Symposium Pesticide Chemistry: Mobility and degradation of Xenobiotics, p. 193-202. Istituto di Chimica Agraria ed Ambientale, Universita Cattolica del Sacro Cuore, Piacenza, Italy.

Haith, D.A. and R.C. Loehr (eds.), 1979. *Effectiveness of soil and water conservation practices for pollution control.* U.S. Environmental Protection Agency, Athens, GA. Report no. EPA-600/3-79-106.

Haude, W., 1952. *Zur Möglichkeit nachträglicher Bestimmung der Wasserbeanspruchung durch die Luft und ihrer Nachprüfung an Hand von Tropversuchen und Abflussmessungen,* Ber. Dtsch. Wetterd. US-Zone, 32, 27-34.

Hutson, J.L. and R.J. Wagenet, 1992. 'Leaching Estimation And Chemistry Model (LEACHM), a process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone'. Cornell Dept. of Soil, *Crop and Atmosph. Sci,* no 92-3.

Hutson, J.L., 1983. *Estimating hydrological properties of South African soils*. Ph.D. thesis. University of Natal, Pietermaritzburg, South Africa.

Jarvis, N., 1991. MACRO - *A model of water movement and solute transport in macroporous soil*. Swedish university of agricultural sciences. Department of soil sciences. Reports and dissertations. 9.

Jones, R.L., G.W. Black and T.L. Estes, 1986. 'Comparison of computer model predictions with unsaturated zone field data for aldicarb and aldoxycarb'. *Environ. Tox. and Chem.* 5, 1027-1037.

Klein, M, 1993. *PELMO Pesticide Leaching Model, Version 1.5*. Benutzerhandbuch. Fraunhofer-institut für Umweltchemie und Ökotoxicologie. Schmallenberg, Germany.

Knisel, W.G. 1980. CREAMS; *A field-scale model for chemicals, run-off, and erosion from agricultural management systems*. Conservation Res. Report No. 26, W.G.Knisel, ed., U.S. Dept. of Agr., Science and Education Administration, 643

Leonard, R.A., W.G. Knisel and D.A. Still, 1987. *GLEAMS: Groundwater Loading Effects of Agricultural Management Systems*. Transactions of the ASAE 30, 1403-1418.

Leonard, R.A., W.G. Knisel, F.M. Davis and A.W. Johnson, 1990. 'Validating GLEAMS with field data for fenamiphos and its metabolites'. *J. of Irrig. and Drain. Engin.* 116, 24-35.

Linden, A.M.A. van der, J.J.T.I. Boesten, A.E. Boekhold, H. van den Bosch, F. Swartjes and M. Leistra, 1995. *Validation of the PESTLA model: Final report; conclusions and recommendations*. RIVM report no. 715802005. National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.

Ministerie LNV, 1991. *Meerjarenplan Gewasbescherming*. Regeringsbeslissing (Long-term crop protection plan. Governmental decision). 's-Gravenhage, Sdu Uitgeverij. Tweede Kamer der Staten-Generaal, vergaderjaar 1990-1991, 21677, nrs 3-4. 298 p.

Mueller, T.C., R.E. Jones, P.B. Bush and P.A. Banks, 1992. 'Comparison of PRZM and GLEAMS computer model predictions with field data for alachlor, metribuzin and norflurazon leaching'. *Environ. Tox. and Chem.* 11, 427-436.

Parrish, R.S., C.N. Smith and F.K. Fong, 1992. 'Tests of the Pesticide Root Zone Model and the aggregate model for transport and transformation of aldicarb, metolachlor and bromide'. *J. Environ. Qual.* 21, 685-697.

Pennell, K.D., A.G. Hornsby, R.E. Jessup and P.S.C. Rao, 1990. 'Evaluation of five simulation models for predicting aldicarb and bromide behaviour under field conditions'. *Water Resour. Res.* 26, 2679-2693.

Sauer, T.J., K.J. Fermanich and T.C. Daniel, 1990. 'Comparison of the pesticide root zone model simulated and measured pesticide mobility under two tillage systems'. *J. Environ. Qual.* 19, 727-734.

Smith, M.C., A.B. Bottcher, K.L. Campbell and D.L. Thomas, 1991. *Field testing and comparison of the PRZM and GLEAMS models.* Trans. of the ASAE 34, 838-847.

Wagenet, R.J. and J.L. Hutson, 1986. 'Predicting the fate of nonvolatile pesticides in the unsaturated zone'. *J. Environ. Qual.* 15, 315-322.

Walker, A. and J.A. Thompson, 1977. 'The degradation of simazine, linuron and propyzamide in different soils'. *Weed Research* 17, 399-405.

Walker, A. and A. Barnes, 1981. 'Simulation of herbicide persistence in soil: A revised computer model'. *Pesticide Science.* 12, 123-132.

Walker, A, 1987. 'Evaluation of a simulation model for prediction of herbicide movement and persistence in soil'. *Weed Research.* 27, 143-152.