Comparing and evaluating pesticide leaching models
Results of simulations with PELMO

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Abstract

The PELMO model was used independently by five modellers to reproduce the results of a lysimeter study performed at Tor Mancina in Italy and a field study performed at Vredepeel in the Netherlands. For the comparisons of the Tor Mancina data set the main features of the measured fluxes of water and bromide were well reproduced by the simulations. The deviations between simulated and experimental cumulative amounts of water leached were generally less than 50%. The measured leaching of metolachlor was small (typical concentrations considerably below 0.1 \textmu g/l). These trace amounts were not reproduced by any of the simulations, not even by those calibrated for bromide leaching in the re-packed lysimeters.

For Vredepeel, the agreement between the measured and simulated water tables were generally poor, even on a qualitative level. This was mainly due to PELMOs inability to deal with shallow, fluctuating groundwater tables. Concentrations of both the tracer and the pesticides were generally satisfactorily reproduced in the initial phases of the experiment but not at later stages. In most cases, the penetration depth of the centre of mass was over-estimated by the model and the dispersion of the pesticide under-estimated.

The correct determination of the parameters to simulate the degradation (and adsorption) of pesticide in the field seemed to be of much greater importance for accurately modelling the transport of such chemicals in soils than improvements in the water balance. The degradation data from long-term laboratory studies clearly did not reflect field conditions.

Additional sampling dates to determine more concentration profiles and to measure DT50 values from the field would have helped reducing the differences in picking different input data by the

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modellers and would have improved the accuracy of the model predictions. Validation tests, user guidance and good modelling practice are recommended as essential tools to improve the confidence of the scientific community in modelling results. © 2000 Elsevier Science B.V. All rights reserved.

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1. **Introduction**

Presently, a number of computer models are used to assess the fate of pesticides in different compartments of the environment. A lot of experience has been gained with some models particularly in the field of groundwater protection (Boesten et al., 1995). The German authorities involved in the registration of pesticides ask for lysimeter studies dependent on the results of simulations performed with a pesticide leaching model (Klein, 1995; Klein et al., 1997). Compared with performing field experiments, the use of computer models is relatively cheap and less time-consuming. However, the models have to be examined carefully as to their predictive abilities. Information on the range of validity and status of validation should enable users to judge whether or not the model is suited for the intended use.

The aim of this study was to evaluate the accuracy of PELMO using the results of differently designed field experiments performed in Italy and the Netherlands.

However, as the different users selected the input parameters independently, the influence of the model user on the results of computer models could also be analysed in this study.

The PELMO model was used by five modellers to reproduce the Tor Mancina and the Vredepeel data. Hosang and Klein tested PELMO against the Tor Mancina data (Francaviglia and Capri, 2000), Erzgräber, Resseler, Schäfer and Klein used the Vredepeel data set (Boesten and van der Pas, 2000) to analyse PELMO's capability to predict pesticide concentrations on the field scale. Given the different nature of the Tor Mancina and the Vredepeel experiments, different output quantities were measured. The Tor Mancina data set is based on four lysimeters. During the experiment, the leachate from each lysimeter was collected and analysed for bromide and metolachlor. The Vredepeel data set describes a field study performed in the Netherlands. In this experiment, soil cores were taken at different times to obtain soil moisture and concentration profiles for bromide, bentazone and ethoprophos. The modelling procedure was performed according to Vanclooster et al. (2000) for both data sets.

2. **The PELMO model**

PELMO is a compartment model simulating chemical movement in the unsaturated soil system within and below the plant root zone. Time varying transport, including advection and dispersion are represented in the program. PELMO is based on the PRZM-
1 model (Carsel et al., 1984), but processes were added to overcome limitations of PRZM-1.

Water balance equations are separately developed for the surface zone, horizons comprising the active root zones, and the remaining lower horizons within the unsaturated zone:

Surface zone:

\[(SW)^{t+1}_i = (SW)^{t}_i + P + SM - l_i - E_i\]

Root zone:

\[(SW)^{t+1}_i = (SW)^{t}_i + l_{i-1} - U_i - l_i\]

Below root zone:

\[(SW)^{t+1}_i = (SW)^{t}_i + l_{i-1} - l_i\]

where \((SW)^{t}_i\) is the soil water in layer \(i\) on day \(t\) (cm), \(P\) the precipitation (cm per day), \(SM\) the snow melt (cm per day), \(E_i\) the evaporation from layer \(i\) (cm per day), \(U_i\) the transpiration from layer \(i\) (cm per day), \(l_i\) the percolation out of zone \(i\) (cm per day). Water that infiltrates in the soil is redistributed in such a way that excess water in one layer is always guided downward until all layers are at or below field capacity. A program switch is used to decide whether drainage of the individual compartments occurs instantaneously (free drainage option) or at a rate given by a drainage rate parameter.

\[\Theta^{t+1}_i = (\Theta^{t*}_i - \Theta_{FCi})\exp(-\alpha\Delta t) + \Theta_{FCi}\]

where \(\Theta^{t*}_i\) is the soil water content in layer \(i\) on day \(t\) plus any percolation from the soil layer \(i-1\) before the occurrence of any drainage \((m^3 \cdot m^{-3})\), \(\Theta^{t}_i\) the soil water content in layer \(i\) at the end of day \(t\) \((m^3 \cdot m^{-3})\), \(\Theta_{FCi}\) the soil water content at field capacity in layer \(i\) \((m^3 \cdot m^{-3})\), \(\alpha\) the drainage rate parameter (per day), and \(\Delta t\) the time step (1 day).

If sand and clay content are known, field capacity is estimated by PELMO using the following equation:

\[\Theta_{FC} = \frac{(F_{CL} \times 60 + F_{SA} \times 20 + F_{SI} \times 40)}{10000}\]

where \(\Theta_{FC}\) is the field capacity \((cm^3 \cdot cm^{-3})\), \(F_{CL}\) the clay content (%), \(F_{SI}\) the silt content (%), and \(F_{SA}\) the sand content (%).

The potential evapotranspiration can either be entered as a daily number or calculated according to the equations of Haude or Hamon.

The Haude equation yields

\[E_{pot} = \frac{f_{Haude}ES_{14}(100 - RH)}{100}\]

where \(E_{pot}\) is the daily potential evapotranspiration (mm per day), \(f_{Haude}\) the monthly Haude factor (mm h Pa$^{-1}$), \(ES_{14}\) the saturated vapour pressure at 2.00 p.m. (h Pa), and \(RH\) the relative air humidity in air at 2.00 p.m.
The Hamon equation yields

\[ E_{pot} = \frac{0.021 L_d^2 E_S \cdot 0.21}{T + 273} \]

where \( E_{pot} \) is the daily potential evapotranspiration (mm per day), \( L_d \) the possible hours of sunshine per day (h), \( E_S \) the saturated vapour pressure at the mean air temperature (h Pa), and \( T \) the mean air temperature (°C).

The daily actual evapotranspiration is divided among evaporation from canopy, soil evaporation, and crop transpiration. Total demand is first estimated and then extracted sequentially from crop canopy storage and from each layer until wilting point is reached in each layer or until total demand is met. Evaporation occurs down to a user specified depth (i.e. minimum depth for evaporation). Crop transpiration is met from the layers between this depth and the active rooting depth.

Soil temperatures are estimated based on daily air temperatures by an empirical model according to the following equation:

\[ T_{t+1} = T_t + (T_{t+1,\text{air}} - T_t)0.346 \exp(-0.027028 \times d) \]

where \( T_t \) is the soil temperature on day \( t \) (°C), \( T_{t,\text{air}} \) the mean air temperature on day \( t \) (°C), and \( d \) the depth of the soil layer (cm).

Sorption of pesticides is estimated according to the Freundlich equation

\[ k_d = k_f c_{sol}^{1/(1/n)-1} \]

where \( k_f \) is the sorption constant in Freundlich equation ((μg/g)/(μg/ml)), \( c_{sol} \) the pesticide in soil water (μg/ml), \( 1/n \) the Freundlich exponent, and \( k_d \) the sorption constant ((μg/g)/(μg/ml)).

Increase of sorption with time is estimated using a linear model

\[ k_{di+1} = \frac{k_{di} \times F_{\text{time}}}{100 \times 360} \]

where \( k_{di} \) is the sorption constant of day \( i \) after the 1st application, \( k_{di+1} \) the sorption constant of day \( i + 1 \) after 1st application, and \( F_{\text{time}} \) the annual increase of sorption (%).

In order to consider the influence of soil temperatures on biodegradation PELMO uses the \( Q_{10} \) rule which means that an increase of temperature (e.g. 10°C) leads to a fixed increase in degradation (e.g. factor of 2) mathematically expressed by using a power function as shown in the following equation:

\[ k_{\text{Temp}} = Q^{(T-T_0)/10} \]

where \( k_{\text{Temp}} \) is the correction factor for biodegradation on the basis of the current temperature, \( Q \) the factor for increase of degradation rate given a temperature increase of 10°C, \( T_0 \) the temperature during the biodegradation test (°C), and \( T \) the actual soil temperature (°C).

In addition to the influence of soil temperatures the half-life of a pesticide also depends on the soil moisture. PELMO is able to correct the rate constant based on the model developed by Walker (1987). The user can decide whether the correction is based on the
absolute soil moisture (original Walker approach) or the relative soil moisture (soil moisture related to field capacity). In this study, the original model of Walker was used because the reliability of this empirical model has been shown by a lot of studies in the literature. It is recommended to use the correction based on relative soil moisture only if sufficient experimental data are available. The equation considering absolute soil moisture yields

\[ k_{moi} = (\theta_0/\theta)^e \]

where \( k_{moi} \) is the correction factor for biodegradation on the basis of the current soil moisture, \( \theta \) the current soil moisture content (vol.%), \( \theta_0 \) the soil moisture during degradation test (vol.%), and \( e \) an exponent.

Volatilisation of pesticides is based on Henry’s and Fick’s law, using Henry’s constant and the diffusion coefficient in air. To estimate the amount of pesticide which moves from the soil surface into the atmosphere, the assumption is made that the concentration of the pesticide in the air above the soil is low. Furthermore, the user has to enter the thickness of the active layer \( d \). Finally, PELMO considers only volatilisation from soil water (and not from the sorbed phase). Based on these assumptions volatilisation is calculated according to the following equation:

\[ J_V = -D \times \frac{Hc_1}{d} \]

where \( D \) is the diffusion coefficient in air (cm
\(^2\) per day), \( J_V \) the volatilisation rate (g cm
\(^{-2}\) per day), \( d \) the active layer (cm), \( H \) the Henry’s constant (\(-\)), and \( c_1 \) the dissolved pesticide concentration in the surface layer (g/cm).

Plant uptake of pesticides is estimated to follow a linear model

\[ J_{UPi} = F_{UP} \times c_i \times ET_i \]

where \( F_{UP} \) is the plant uptake factor, \( c_i \) the dissolved pesticide in soil layer \( i \) (g/cm
\(^3\)), and \( ET_i \) the actual evapotranspiration (cm per day).

3. Comparisons between experimental data and simulations

A number of simulations were conducted and compared with the two experimental data sets. These comparisons aimed at showing how well PELMO can predict the measured data without calibration and can be fitted to the measured data. Whereas the first criterion is certainly more relevant from a practical point of view, fitting the model to the experimental data can still help to elucidate the behaviour of the model and explain the discrepancies between the data and the model.

3.1. The Tor Mancina data set

3.1.1. Selection of hydrology-related input parameters

For the simulations the two modellers selected different drainage options. Hosang used the free drainage option, whereas Klein did his simulations based on the restricted
drainage model. Depending on the climatic conditions, more evapotranspiration can be expected when selecting the restricted drainage option because this choice causes the water to reside longer in the top soil layers where it is available for evapotranspiration. The second important difference between the model runs of Klein and Hosang is the setting of the minimum depth down to which evaporation is extracted. Klein used a value of 50 cm whereas Hosang specified 10 cm. Again the selection of Klein leads to more evaporation and therefore less leaching as compared with the simulations of Hosang.

The four simulations of Hosang differ mainly in the way potential evapotranspiration is simulated. In simulation 1, the original Haude equation was used when experimental data on evapotranspiration were not available. In the other simulations, the Haude equation with original parameters (simulations 2 and 4) or calibrated parameters (simulation 3) have been selected, irrespective of experimental data availability. In simulation 3, the Haude parameters, which were derived under Mid-European conditions, were modified to reflect the Italian climate. For calibration purposes Hosang modified the field capacity (which was given for the lysimeter soil) from 31% to an unrealistic value of 62% in simulation 4. The purpose of changing this parameter was not to reflect realistically the experimental conditions but merely to fit the data. Doubling the field capacity reduces the amount of leaching because of increased water retention in the soil profile and hence more evapotranspiration from the top layers. The input parameters selected by the two modellers are given in Table 1.

3.1.2. Selection of chemical-related input parameters

The two modellers generally selected the same input parameters for bromide (DT50: infinite, sorption coefficient: 0 l/kg). However, there was one exception: in contrast to Hosang, Klein considered uptake of bromide by plants. As all important input parameters for metolachlor were provided by Francaviglia and Capri (2000) both modellers used exactly the same input data. Differences in the model output are therefore caused by input parameters that control the hydrological processes.

Table 1
Hydrology-related input parameters and model switches (Tor Mancina data set)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hosang 1</th>
<th>Hosang 2</th>
<th>Hosang 3</th>
<th>Hosang 4</th>
<th>Klein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodynamic dispersion</td>
<td>0 cm per day</td>
<td>0 cm per day</td>
<td>0 cm per day</td>
<td>0 cm per day</td>
<td>0 cm per day</td>
</tr>
<tr>
<td>Drainage switch</td>
<td>Free</td>
<td>Free</td>
<td>Free</td>
<td>Free</td>
<td>Restricted</td>
</tr>
<tr>
<td>Drainage rate parameter</td>
<td>Not applicable</td>
<td>Not applicable</td>
<td>Not applicable</td>
<td>Not applicable</td>
<td>1.0 per day</td>
</tr>
<tr>
<td>Initial water content</td>
<td>35%</td>
<td>35%</td>
<td>35%</td>
<td>35%</td>
<td>30%</td>
</tr>
<tr>
<td>Field capacity</td>
<td>31%</td>
<td>31%</td>
<td>31%</td>
<td>62%</td>
<td>31%</td>
</tr>
<tr>
<td>Minimum depth for</td>
<td>10 cm</td>
<td>10 cm</td>
<td>10 cm</td>
<td>10 cm</td>
<td>50 cm</td>
</tr>
<tr>
<td>evapotranspiration</td>
<td>Experimental data (Haude)</td>
<td>Haude</td>
<td>Calibrated (Haude)</td>
<td>Haude</td>
<td>Experimental data (Hamon)</td>
</tr>
<tr>
<td>Potential depth for</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>evapotranspiration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1.3. Results

3.1.3.1. Water and bromide. Fig. 1 clearly shows that the cumulated leachate is overestimated by all model simulations. However, the simulation of Klein and Hosang’s (simulation 4) reflect the experimental results quite well. Similar results were found for the irrigation scheme 2 (lysimeters 11 and 13).

Calibration of a model should reflect the physical, chemical and biological characteristics of the soil, which is to be described as closely as possible. Setting a parameter to a specific value merely to achieve a good fit to the measured data should be avoided. Klein’s decision to choose the restricted drainage option seems reasonable in this respect, in view of the low sand contents of the packed lysimeter soils (20%). However, selecting the restricted drainage option requires specifying the drainage rate, which has no physical significance (as opposed to e.g. hydraulic conductivity, which is a measurable property). Moreover, as PELMO does not allow for upward water flow, the maximum depth down to which water can be withdrawn by evapotranspiration has to be estimated. No physical significance can be attributed to this parameter either and only an arbitrary estimation is possible.

Hosang used field capacity as a fitting property. At first sight, this seems to contradict the principle of not changing any parameters which reflect some observable property of the soil. However, field capacity is not a physically defined property and has only an operational significance (e.g. Jury et al., 1991). So, PELMO cannot be run without

Fig. 1. Comparison of simulated and experimental leachate in Tor Mancina (IRR 1).
specifying ‘non-physical’ parameters and the two modellers have merely chosen different ways of dealing with this difficulty.

Fig. 2 shows that the simulations which gave good results for the leaching of water (see Fig. 1) also did so for bromide. Klein’s simulation fits best, but only after additional calibration (plant uptake factor for bromide of 0.1). These results could be confirmed by the simulations with irrigation scheme 2 (lysimeters 11 and 13, no graphical representation).

3.1.3.2. Metolachlor. All simulations with metolachlor resulted in no leaching of this substance, whereas the measured data show that trace quantities leached ranged from 0.052 to 0.077 g ha$^{-1}$ (0.002–0.003%). Two possible reasons may account for this discrepancy between the model and the data. Either the trace amounts (typical concentrations are much below the µg/l level) were caused by preferential flow, which is not allowed for by PELMO or the degradation and adsorption behaviour in the outdoor study was not adequately reflected by the pesticides properties used for the calculations.

3.2. The Vredepeel data set

3.2.1. Selection of hydrology-related input parameters

The selection of hydrology-related input parameters was quite similar amongst the different users. All modellers used the free drainage model of PELMO and set the hydrodynamic dispersions to 0 cm per day. They also used the same value for the minimum depth for evaporation (10 cm), and the same method to estimate field capacity based on sand and clay content. However, Klein used a more sophisticated method for estimating potential evapotranspiration, i.e. an external calculation using the Doorenbos
and Pruitt (1977) approach. The calibrated simulation of Erzgräber was based on Makkink reference data. The other modellers were using the Haude approach.

3.2.2. Selection of chemical-related input parameters

The simulations by the various modellers differ mostly in the selection of pesticide input parameters. Among Klein’s simulations, one variation is based on Klein’s interpretation of the adsorption and degradation data provided whereas in the second run the input parameters suggested by van den Bosch and Boesten (1994) were used.

PELMO is able to model an increase of adsorption with time. Only Klein used this option to describe the adsorption behaviour of ethoprophos. Klein was also the only modeller who used PELMO’s volatilisation routine to allow for the rapid dissipation of ethoprophos at the beginning of the experiment (diffusion coefficient for ethoprophos 0.05 cm per day). He calibrated the volatilisation process by setting the thickness of the stagnant surface layer to 1 mm.

In contrast to the Tor Mancina simulations the chemical input parameters used for the various Vredepeel simulations differed widely. Rather than providing the modellers with DT50 values, $Q_{10}$ factors and Freundlich adsorption parameters, the data set providers made only the detailed results of the adsorption and degradation studies available. Depending on the evaluation of the experimental data, the modellers estimated different degradation and adsorption parameters. In particular, the analyses of the degradation study resulted in very different half-lives (Tables 2 and 3).

The DT50 values and $Q_{10}$ factors given in Tables 2 and 3 are mutually dependent. A low DT50 value at a given reference temperature may be compensated by a high $Q_{10}$ factor to result in the same DT50 at the temperature of interest. Therefore both factors have to be taken into account simultaneously (Figs. 3 and 4). The temperature dependency represented by Klein’s parameters fits the data most closely. However, the exact positions of the experimental DT50 values (the circles in the figures) depend upon

![Fig. 3. Bentazone: half-life as a function of temperature.](image-url)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Resseler 1</th>
<th>Resseler 2</th>
<th>Klein</th>
<th>Klein (van den Bosch and Boesten, 1994)</th>
<th>Schäfer</th>
<th>Erzgräber</th>
<th>Erzgräber (calibrated)</th>
<th>Recommended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of application (kg/ha)</td>
<td>0.63</td>
<td>0.63</td>
<td>0.8</td>
<td>0.63</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.63</td>
</tr>
<tr>
<td>DT50 at 10°C (day)</td>
<td>87.3</td>
<td>33.8</td>
<td>104</td>
<td>86.9</td>
<td>50</td>
<td>71.07</td>
<td>71.07</td>
<td>136</td>
</tr>
<tr>
<td>Q10 factor</td>
<td>5.42</td>
<td>2.1</td>
<td>3.9</td>
<td>5.4</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>2.22</td>
</tr>
<tr>
<td>Reference soil moisture (%)</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>20</td>
<td>17</td>
<td>17</td>
<td>–</td>
</tr>
<tr>
<td>Moisture exponent</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>–</td>
</tr>
<tr>
<td>Sorption coefficient kf (l/kg)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.09</td>
<td>0.105</td>
<td>0.085</td>
<td>0.11</td>
<td>0.11</td>
<td>0.105</td>
</tr>
<tr>
<td>Freundlich exponent</td>
<td></td>
<td></td>
<td>0.83</td>
<td>0.82</td>
<td>1.0</td>
<td>0.92</td>
<td>0.92</td>
<td>0.82</td>
</tr>
<tr>
<td>Sorption increase (percentage per year)</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
the evaluation of the degradation test. The experimental DT50 values presented in the figures have been calculated according to the method used by Klein (linear regression of time versus the logarithms of residues). So, it comes as no surprise that these half-lives are perfectly represented by Klein’s $Q_{10}$ factor. A different method was used by Schäfer. He took the experimental DT50 at 20°C, but then used PELMOs default $Q_{10}$ factor of 2 instead of estimating it from the experimental data. Resseler used a similar approach in taking the DT50 value (20°C) given by Boesten and van der Pas (2000) as a reference value, a $Q_{10}$ factor of 5.4 calculated from these experiments and, alternatively, a $Q_{10}$ value of 2.1, as recommended by the literature review of the FOCUS soil modelling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Klein</th>
<th>Klein (van den Bosch and Boesten, 1994)</th>
<th>Schäfer</th>
<th>Erzgräber (calibrated)</th>
<th>Recommended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of application (kg/ha)</td>
<td>3.35</td>
<td>1.30</td>
<td>3.35</td>
<td>3.35</td>
<td>3.35</td>
</tr>
<tr>
<td>DT50 at 10°C (day)</td>
<td>227</td>
<td>195</td>
<td>153</td>
<td>166.13</td>
<td>166.13</td>
</tr>
<tr>
<td>$Q_{10}$ factor</td>
<td>2.3</td>
<td>2.5</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Reference soil moisture (%)</td>
<td>19</td>
<td>19</td>
<td>20</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Moisture exponent</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
<td>0.718</td>
</tr>
<tr>
<td>Sorption coefficient $k_f$ (l/kg)</td>
<td>3.57</td>
<td>3.9</td>
<td>3.5</td>
<td>4.29</td>
<td>4.29</td>
</tr>
<tr>
<td>Freundlich exponent</td>
<td>0.87</td>
<td>0.87</td>
<td>0.86</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>Sorption increase (percentage per year)</td>
<td>500</td>
<td>500</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Henry’s constant (J/mol)</td>
<td>$1.52 \times 10^{-2}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

![Fig. 4. Ethoprophos: half-life as a function of temperature.](image-url)
workgroup (Boesten et al., 1996), as a standard default value. Looking at the wide range of pesticide parameter values used, it has been decided to conduct simulations with the parameter set recommended by the data set provider. For ethoprophos this recommended set closely followed the degradation parameters selected by Klein (van den Bosch and Boesten, 1994) whereas for bentazone no modeller was close to the recommendations by the data set provider.

3.2.3. Results

3.2.3.1. Water and bromide. The hydrological situation in the Vredepeel field is characterised by a seasonally fluctuating ground water table. This cannot be simulated adequately by capacity models like PELMO. As shown in Fig. 5A and C for March 1991 and 1992, all PELMO calculations predict a relatively homogeneous soil moisture profile near field capacity. As opposed to this, the observed soil moisture shows a clear depth dependency with higher values in the capillary fringe above the groundwater table. As shown in Fig. 5B, in August 1991, the situation is different. Klein’s simulation fits well whereas the simulation of Schäfer results in water contents which are too large in most parts of the profile. The soil moisture calculated by Erzgräber who used the Makkink reference data was closer to the observed values, but also showed a tendency to over-estimate.

The quality of soil moisture predictions during the warm season strongly depends on the accuracy of the estimated evapotranspiration. Klein used a more sophisticated method for this task (method of Doorenbos and Pruitt) than the other modellers. They employed the method of Haude which is implemented in PELMO. Given the different levels in complexity of these evapotranspiration models, it is not surprising that Klein obtained the best fit to the measurements.

Though Klein’s simulation of soil moisture agrees best with the measured data, this is not true for the estimated bromide concentrations. Fig. 6B and C show that the concentrations at the time of the second and third sampling were clearly over-estimated in all cases. Only the prediction for the first sampling date in March 1991 were in line with the experimental data (Fig. 6A). It seems to be difficult to explain this deviation as the soil moisture has been estimated quite well. However, soil moisture is a static variable. The water fluxes, that were not measured, may be nevertheless different in the experiment and in the simulation.

3.2.4. Bentazone

As the pesticide bentazone is only weakly adsorbed to soil (Table 2), the water flow can be expected to play a key role in its behaviour in soil. So, PELMO which was found to have fundamental difficulties in correctly describing the hydrological situation in the Vredepeel field, can also be expected to do a poor job of describing the behaviour of bentazone.

PELMO does not allow for the increased degradation with time suggested by the experimental data (i.e. the rapid decrease of the concentrations in soil between 27 August 1991 and 10 March 1992, Fig. 7B and C). This may explain the large discrepancies found between the measured and modelled concentration profiles which were particularly
obvious in the simulation, based on the recommended parameter set. This simulation that strictly relied on laboratory-estimated parameters showed the poorest results when comparing with the field data (see Fig. 7A–C).

The simulations, which show the best fit to the experimental results in terms of the peak positions of the concentration profiles, were run by Erzgräber. Resseler’s simulations were best at reproducing the shape of the measured concentration peaks. The model runs with the lower input values for the DT50 and/or application rate showed the best fit to the measured concentration profiles in soil. One explanation for this is that
Fig. 6. Comparison of measured and simulated residues of bromide in soil at Vredepeel on (A) 5 March 1991; (B) 27 August 1991; and (C) 10 March 1992.
the degradation behaviour in the field was not adequately reflected by the laboratory experiments conducted for bentazone at lower temperatures and/or longer incubation times. This resulted in degradation rates that were too low. These experiments were perhaps not able to describe accurately the real behaviour of the compound in the field. Moreover, they could be evaluated in different ways, all of which were equally valid on a
scientific basis. Unfortunately neither the initial concentration of the pesticides in soil nor the dissipation rate in the field have been determined to check the validity of the laboratory experiments and, of course, the resulting model input. Consequently, even expert judgement of the different modellers was not able to identify the underlying mechanisms for e.g. degradation, and resulted in a high variation of the selected input parameters (see Tables 2 and 3 and Figs. 3 and 4).

The large deviations between model and field observations for soil moisture and bromide did not affect the accuracy of the predicted bentazone concentrations. It is surprising that the fate of bentazone in the Vredepeel field was highly influenced by pesticide properties such as degradation and adsorption and not by the hydrology. Correctly measured pesticide parameters seem to be of much greater importance for modelling the transport of degrading and sorbing chemicals in soils, than improvements in the hydrological part of the model derived from measurements with inert tracers. Depending on the selection of these input parameters, the PELMO simulations were generally within a factor of three of the experimental data for concentrations >0.01 mg/dm³.

3.2.4.1. Ethoprophos. From laboratory studies, ethoprophos, unlike bentazone, is known to be strongly adsorbed to soil. This was also observed in the Vredepeel field study where the substance remained in the upper 5 cm of the soil throughout the experiment.

The fate of a pesticide which is strongly adsorbed to soil is not influenced too much by the hydrological conditions. So, it can be speculated that even a computer model which performed poorly for the bromide part of the experiment should be able to predict the fate of ethoprophos, provided that its adsorption and degradation parameters are specified correctly.

The deviations between the different modellers were quite small even though their interpretations of the laboratory measurements varied widely (Table 3). Results from all modellers were relatively close to the field data on 5 March and 27 August (Fig. 8A and B). However, even the run which came closest to the experimental data (Klein’s simulation based on the suggestion of input parameters of van den Bosch and Boesten, 1994) did not reproduce the rapid degradation of ethoprophos between 27 August 1991 and 10 March 1992. The increased degradation observed in the field did not occur in the laboratory and consequently no modeller was able to simulate the behaviour of ethoprophos correctly during this period.

The behaviour of ethoprophos was again best reproduced by Klein’s simulations (Fig. 8A–C). Only in these simulations the mobility of ethoprophos was not over-estimated. There were no significant differences between the adsorption parameters used in the different simulations which could account for the varying results. However, Klein was the only modeller who allowed for increased adsorption with time (linear increase of 500% per year, Table 3). Increased adsorption with time is a well known and surely important phenomenon but, as this process is not routinely measured in the laboratory, there is little specific and quantitative information available. However, the results of the Vredepeel field study clearly demonstrate that without considering adsorption with time, it was not possible to model the movement of ethoprophos adequately.
4. Discussion and conclusions

In this study two data sets were compared with a number of simulations with the PELMO model. The target quantities of the comparison were the fluxes of water, a mobile and non-
reactive tracer and a pesticide in one case (Tor Mancina) and the contents and concentrations of water, a mobile and non-reactive tracer and two pesticides in the other (Vredepeel). The following points can be made for the comparisons for Tor Mancina:

- The main features of the measured fluxes of water and bromide were well reproduced by the simulations. The simulated cumulative amounts of water leached were generally within a factor of 3 of the measured values.
- The measured leaching of metolachlor was very limited (typical concentrations much below 0.1 µg/l). These trace amounts were not reproduced by any of the simulations, not even by those calibrated for bromide leaching in the re-packed lysimeters.

For Vredepeel, the main results can be summarised as follows:

- The agreement between the measured and simulated soil water content was poor, even on a qualitative level. This is due to PELMO’s inability to deal with shallow fluctuating groundwater tables.
- Concentrations of both the tracer and the pesticides were generally better reproduced in the initial phases of the experiment than at later stages. In most cases, the penetration depth of the centre of mass was over-estimated by the model and the dispersion of the pesticide under-estimated. PELMO’s inability to adequately describe the shallow water table situation might be a first explanation for the partially unsatisfactory results for the chemicals. However, looking to the results of the models which solve the more sophisticated Richards’ equation (e.g. PESTLA or LEACHM), similar deviations were found between experimental and simulated data for pesticide fate (Tiktak, 2000).

However, PELMO showed that it is a useful tool to obtain order-of-magnitude estimates of predicted environmental concentrations above trace levels. Calibrating PELMO to the actual hydrological situation certainly improved the agreement between data and model. However, the differences between calibrated and uncalibrated simulations were generally smaller than the differences between different modellers. The correct determination of the parameters to simulate the degradation (and adsorption) of pesticides in the field seemed to be of much greater importance for accurately modelling the transport of such chemicals in soils than improvements in the water balance. The degradation data from long-term laboratory studies for bentazone obviously did not reflect field conditions. Additional sampling dates to determine more concentration profiles and to measure DT50 values from the field would have helped to reduce the differences in selecting different input data by the modellers and would have improved the accuracy of the model predictions. This clearly points to the importance of adequate user guidance on the specification of model parameters and switches (e.g. as given by Resseler et al. (1997) for modelling studies for the registration of pesticides). Validation tests, user guidance and “good modelling practice” should be essential tools to improve the confidence of the scientific community in modelling results.

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