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# Sensitivity analyses for four pesticide leaching models

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**Abstract: Sensitivity analyses using a one-at-a-time approach were carried out for leaching models which have been widely used for pesticide registration in Europe (PELMO, PRZM, PESTLA and MACRO). Four scenarios were considered for simulation of the leaching of two theoretical pesticides in a sandy loam and a clay loam soil, each with a broad distribution across Europe. Input parameters were varied within bounds reflecting their uncertainty and the influence of these variations on model predictions was investigated for accumulated percolation at 1-m depth and pesticide loading in leachate. Predictions for the base-case scenarios differed between chromatographic models and the preferential flow model MACRO for which large but transient pesticide losses were predicted in the clay loam. Volumes of percolated water predicted by the four models were affected by a small number of input parameters and to a small extent only, suggesting that meteorological variables will be the main drivers of water balance predictions. In contrast to percolation, predictions for pesticide loss were found to be sensitive to a large number of input parameters and to a much greater extent. Parameters which had the largest influence on the prediction of pesticide loss were generally those related to chemical sorption (Freundlich exponent $n_f$ and distribution coefficient $K_f$) and degradation (either degradation rates or $DT_{50}$, QTEN value). Nevertheless, a significant influence of soil properties (field capacity, bulk density or parameters defining the boundary between flow domains in MACRO) was also noted in at least one scenario for all models. Large sensitivities were reported for all models, especially PELMO and PRZM, and sensitivity was greater where only limited leaching was simulated. Uncertainty should be addressed in risk assessment procedures for crop-protection products.**


**Keywords:** pesticide; leaching; model; sensitivity; uncertainty; calibration

## 1 INTRODUCTION

Sensitivity analysis of mathematical models consists in investigating the relationship between model input and output.[1] The information derived from sensitivity analyses can be used in several ways. First, analysis of the sensitivity of a model can be considered an essential part of its development[2,3] and evaluation,[3,4] since it provides the modeller with an opportunity to identify deficiencies in the theoretical structure of models[5] and problems in their operation.[2] Second, sensitivity information can be used for model simplification and refinement.[6] For instance, if a parameter has been shown to have little effect on the model outcome, the model may be simplified by making this parameter a constant[5] or eliminating those terms utilising the parameter.[2] Third, it can help to identify those parameters which require the greatest accuracy in their determination[7] and which require the most (or least) attention when parameterising models.[8,9] Also, sensitivity information is useful to select the relative priority of parameters to be varied when model calibration is undertaken[10,11] or to be included in probabilistic modelling.[12] Fourth, sensitivity information is useful to interpret model output effectively[4,6] and improve the credibility of modelling results.[13] Finally, the information can be used for guiding effort in data collection for deriving model input parameters,[14] designing field studies,[4] but also for identifying areas where additional research and further model development is needed.[2,15]

A wide range of models are used to assess the environmental fate of crop-protection products and, particularly, their potential transfer to surface and ground water following an application to an agricultural field. Four models have mainly been used in Europe in the last five to ten years for assessing the potential for leaching to groundwater within the scope of pesticide registration: PRZM,[16,17] PELMO,[18,19] PESTLA[20,21] and MACRO.[22,23] PESTLA has recently been superseded by PEARL[24] although most of the model descriptions remain broadly the same. Some information on the sensitivity of these models exists.[2,4,5,7,9,20,22,25–27] However, the information is difficult to use in practice

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because sensitivity analyses have been conducted using a range of techniques and results may not be directly comparable from one study to another,[2,7,9] (2) may have concentrated on a few input parameters only,[7,22,25] and (3) may have been generated for one particular scenario only.[5,22] Information on sensitivity analysis is of limited benefit at lower tiers of the risk assessment where fixed assumptions and scenarios are considered. However, the information becomes of real value at higher tier levels where tailored complex modelling is carried out to predict the fate of pesticides.

In order to provide results with a wide applicability, sensitivity analyses were carried out for PELMO, PRZM, PESTLA and MACRO using a standardised procedure for the four models. A simple approach to sensitivity analysis was adopted where each parameter was varied one after the other, all other parameters being kept at their nominal values (one-at-a-time sensitivity analysis). A total of four leaching scenarios were generated and model input parameters were varied within bounds reflecting their uncertainty. Input parameters for the four models were ranked according to their influence on model predictions for water percolation and pesticide loss by leaching.

## 2 MODELLING METHODS

### 2.1 Base-case scenarios

Results of sensitivity analyses for environmental models are known to be site and condition specific.[8] Four base-case scenarios were thus considered in this study to encompass a range of environmental conditions with respect to pesticide leaching. The scenarios were compiled by simulating the fate of two hypothetical pesticides in two soils.

Sorption and degradation properties for the two theoretical pesticides were chosen to allow significant leaching of the compounds at 1-m depth. Pesticide 1 has a $K_{oc}$ value of 20 ml g$^{-1}$ and a laboratory $DT_{50}$ of 7.8 days at 20 °C whilst Pesticide 2 has a $K_{oc}$ of 100 ml g$^{-1}$ and a laboratory $DT_{50}$ of 23.3 days at 20 °C. Degradation of the two compounds was assumed to follow first-order kinetics. Although hypothetical, the properties of the two compounds fall within the range of those registered for use in Europe.[9]

Modelling was undertaken for a sandy loam and a clay loam soil to give contrasting behaviour with respect to contaminant transfer. Specific soils were selected within the broad categories on the basis of their use in an earlier study.[28] Soils from the Wick series are deep, uniformly coarse textured, free-draining sandy loams formed on loose, sandy or sandy gravelly glacial, fluvioglacial or river terrace deposits.[29] They have low water retention and, under arable cultivation, low organic matter contents and therefore readily transmit a wide range of pollutants. Soils from the Wick series and their hydrological equivalents in Europe are presented in Fig 1 and cover 190 000 km$^2$ (4% of the European land area shown on Fig 1).[30] Soils from the Hodnet series are deep, fine loamy, reddish soils formed on interbedded reddish sandstones and mudstones.[29] They have

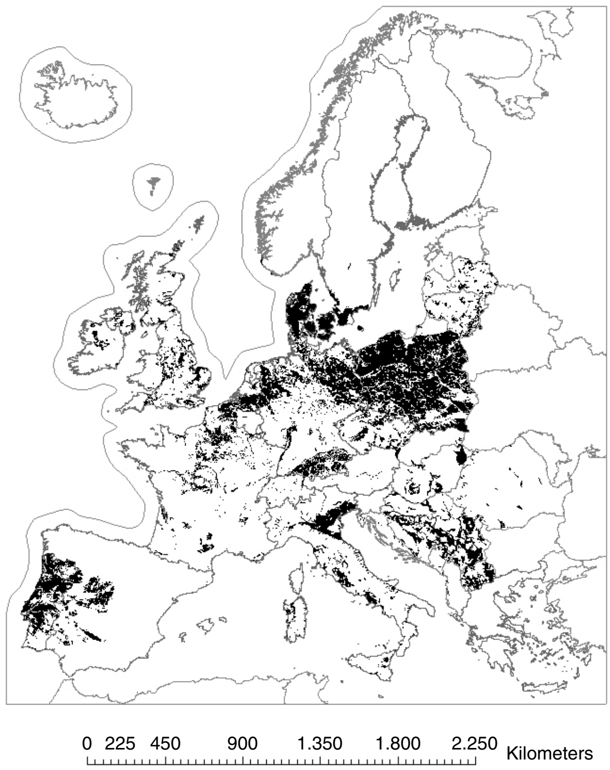


**Figure 1.** Wick soils and their hydrological equivalents in Europe. Hydrological equivalents were taken as free-draining, uniformly textured coarse Cambisols, Fluvisols, Arenosols and Regosols.

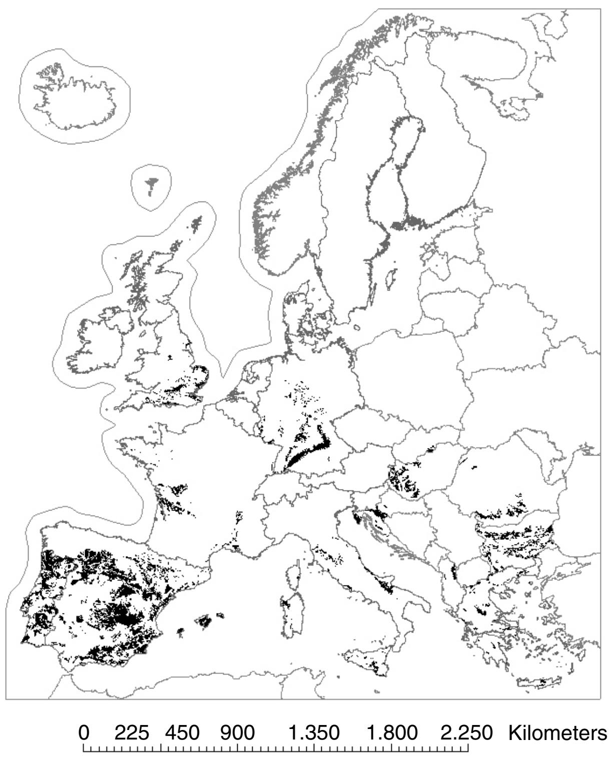


**Figure 2.** Hodnet soils and their hydrological equivalents in Europe. Hydrological equivalents were taken as all medium loamy and silty chromic Luvisols.

**Table 1.** Physico-chemical and hydraulic properties for the two soils selected for the modelling

| | Wick | | | | Hodnet | | | |
|---|---|---|---|---|---|---|---|---|
| | 0–20 cm | 20–50 cm | 50–75 cm | 75–100 cm | 0–33 cm | 33–60 cm | 60–80 cm | 80–100 cm |
| *Physico-chemical properties* | | | | | | | | |
| Organic carbon (%) | 1.70 | 0.80 | 0.30 | 0.20 | 1.15 | 0.48 | 0.40 | 0.30 |
| Bulk density (g $cm^{-3}$) | 1.35 | 1.45 | 1.41 | 1.53 | 1.39 | 1.62 | 1.55 | 1.48 |
| Sand (%) | 57 | 70 | 73 | 77 | 33 | 42 | 29 | 26 |
| Silt (%) | 33 | 20 | 16 | 9 | 48 | 42 | 48 | 55 |
| Clay (%) | 10 | 10 | 11 | 14 | 19 | 16 | 23 | 19 |
| Texture[a] | SL | SL | SL | SL | CL | ZCL | CL | CL |
| *Water retention data*[b] | | | | | | | | |
| $W_{0kPa}$ (%) | 46.6 | 39.6 | 39.0 | 34.3 | 46.8 | 38.8 | 41.5 | 44.0 |
| $W_{5kPa}$ (%) | 27.8 | 19.1 | 14.7 | 19.2 | 34.9 | 30.8 | 32.2 | 35.8 |
| $W_{10kPa}$ (%) | 24.1 | 17.0 | 11.7 | 16.4 | 33.7 | 29.9 | 31.4 | 35.0 |
| $W_{40kPa}$ (%) | 19.7 | 14.2 | 8.7 | 13.4 | 31.2 | 26.7 | 28.9 | 31.8 |
| $W_{200kPa}$ (%) | 15.1 | 10.8 | 6.0 | 9.8 | 25.1 | 24.2 | 24.5 | 26.6 |
| $W_{1500kPa}$ (%) | 10.5 | 7.9 | 4.4 | 7.7 | 16.8 | 17.9 | 19.9 | 20.1 |

[a] Texture given according to the UK classification; SL: sandy loam; CL: clay loam; ZCL: silty clay loam.
[b] Volumetric water content at a given pressure.

slowly permeable horizons in the subsoil which restrict the downward percolation of water and these soils are occasionally waterlogged. Soils from the Hodnet series and their hydrological equivalents in Europe are presented in Fig 2 and represent 43 000 $km^2$ (1% of the European land area shown on Fig 2).[30] Selected physico-chemical properties and water retention data for the two soils are presented in Table 1. A 1-m deep profile was simulated for both soils to allow direct comparison of leaching to depth and to tie with current practices in risk assessment for pesticides in groundwater within the EU.[31]

A winter wheat crop was simulated in each year and emergence, maturation and harvest dates were set to 12 October, 24 June and 7 August, respectively.[32] Both compounds were considered to be applied on 1 November in the first year only at an application rate of 2.0 kg $ha^{-1}$. No correction was made to account for interception of the sprayed solution by the crop.

Weather data were selected from long-term records for Silsoe (Bedfordshire, UK; latitude 52.0 °N, longitude 0.4 °W). The year 1979 was chosen from a 30-year (1965–1994) dataset as being wetter than average (700 mm of rainfall compared to a 30-year mean of 575 mm; 97th percentile), especially in the winter and the spring periods. This volume of rainfall is typical for large parts of Europe. Potential evapotranspiration (PET) was calculated outside the models using the Penman–Monteith equation.[33] The data for 1979 were repeated for 10 years. The reason for repeating a year rather than taking real meteorological data for 10 years is that models were run for the minimum time that encompassed full leaching breakthrough (ie predicted concentrations returned to zero) of the two pesticides. Having the same weather data between years meant that the comparison between modelling scenarios with different duration was still meaningful.

### 2.2 Modelling strategy and automation of modelling tasks

Sensitivity investigations concentrated on the four models which have been used extensively in Europe for the assessment of leaching within the scope of pesticide registration. These were the PEsticide Leaching MOdel (PELMO; version 3.00, July 1998),[18,19] the Pesticide Root Zone Model (PRZM; Version 3.14$\beta$, January 2000),[16,17] the PESTicide Leaching and Accumulation model (PESTLA; version 3.4, September 1999)[20,21] and the MACRO model (version 4.1, July 1998).[22,23] The Dutch model PESTLA has been extensively used for registration purposes in The Netherlands and other European countries in the last few years, but has recently been superseded by PEARL (Pesticide Emission Assessment at Regional and Local scales) following its release in 2000.[24] Comparison tests were undertaken for the Dutch standard scenario and showed that PESTLA and PEARL predicted the same concentrations at levels $>1$ µg $litre^{-1}$ while slightly larger concentrations were obtained with PEARL when smaller concentrations levels ($<0.1$ µg $litre^{-1}$) were simulated. Differences reported for the standard scenario were attributed to changes to the definition of the scenario (bottom boundary condition) and to alterations to the numerical description of transformation processes and soil temperatures.[24] Specific versions of selected pesticide leaching models (commonly termed 'FOCUS versions') have recently been released by the FOCUS groundwater scenarios working group to enable first-tier assessments of the potential for leaching to depth in Europe.[31] These releases were not available at the time the sensitivity analyses were carried out and investigations were undertaken on the very latest versions of the models available at the time. Although the models used here predated FOCUS releases, it can be considered that they are similar in their behaviour to those implemented in the FOCUS framework.

The PELMO model was developed from an early version of PRZM and the two models are hence quite similar. They both rely on a description of soil hydrology based on a 'tipping-bucket' approach where water will only move to the next soil layer if field capacity is exceeded. Solute transport is simulated using the convection–dispersion equation. Both models implement the Freundlich equation for describing sorption and assume first-order kinetics for degradation. PRZM also enables the use of a bi-phasic equation for this latter process. Soil erosion is simulated using the universal soil loss equation, while a modified Soil Conservation Service curve number technique is used for run-off. Both PRZM and PELMO can simulate the loss of pesticide resulting from volatilisation. PESTLA implements Richards' equation and the convection–dispersion equation for simulating water flow and solute transport, respectively. As for PRZM and PELMO, the Freundlich equation and first-order kinetics are used to simulate sorption and degradation, respectively. Volatilisation and loss of pesticides to drainage are simulated, but not soil erosion and run-off. The model includes a range of bottom boundary conditions and can simulate the fluctuation of a water table in the profile. MACRO is the only one of the four models which includes a description of preferential flow processes by dividing the total soil porosity into two flow domains (micropores and macropores). Soil water flow and solute transport in the micropores is simulated using Richards' equation and the convection–dispersion equation, respectively, while fluxes in the macropores are based on a simpler capacitance-type approach with mass flow. Sorption is simulated using the Freundlich equation and the distribution of the sorption sites between micropores and macropores must be specified. First-order kinetics is used to simulate degradation and half-lives need to be provided for the solid and liquid phase of the micropores and macropores. MACRO can simulate losses by drainage, but does not include a description of volatilisation processes. As for PESTLA, a range of bottom boundary conditions is available. Further comparison of the process descriptions in the four models can be found elsewhere.[34]

Models were parameterised to simulate the leaching of the two pesticides in the two soils. Run-off, erosion and volatilisation subroutines were switched off in the modelling. The bottom boundary condition needs to be specified in PESTLA and MACRO and this was set to a free draining profile. Increase of sorption with time was not simulated to maintain consistency of results between those models which provide a description of this feature and those which do not. No calibrations were undertaken to attempt to match model predictions for water leaching and pesticide loss between the four models. The parameterisation of the models was based on measured properties as much as possible. Simulations were carried out until full leaching of the two pesticides was achieved or for a set period where running time was not a limiting factor. This resulted in differences in the number of years run between models and scenarios. However, comparison of sensitivity results between different scenarios remained meaningful because of the use of repeated weather data. The input files for the four leaching scenarios and associated model predictions for water leaching and pesticide loss are referred to as 'base-case simulations' henceforth.

For all models, degradation rates were supplied to the models as laboratory values and model subroutines for corrections of degradation for moisture and temperature effects were therefore activated. Degradation at depth was related to that in the topsoil using the equation reported by Jarvis *et al*,[35] which accounts for the decrease in microbial activity with depth and the change in pesticide availability arising from sorption in the different horizons. Sorption was assumed to be proportional to organic carbon content in the different horizons and to be described by a non-linear Freundlich isotherm ($n_f = 0.9$). Sorption distribution coefficients ($K_d$) were introduced directly into the model, except for PESTLA for which a $K_{om}$ (sorption coefficient normalised to organic matter) value for the topsoil was used. The need to minimise running time within the scope of the present exercise which involved a large number of model runs meant that the pre-run duration was limited to the time between the start of the year and the pesticide application in the first year (11 months). Initial moisture contents in the different horizons at the start of the simulations were set to field capacity values.

Modelling tasks were automated using the SENSAN (SENSitivity ANalysis) tool which is part of the inverse modelling PEST package.[36] The package facilitates the sensitivity analysis process by automating the tasks of adjusting specific model inputs, running the models, recording their values, archiving the output files and then recommencing the whole cycle. SENSAN interferes with models using their input and output files only and is broadly model independent. It was thus possible to link SENSAN to the four pesticide leaching models without altering their code.

## 2.3 Approach to sensitivity analysis

Model sensitivity can be assessed using a range of techniques varying in their complexity and sophistication.[6,15] Differences between the techniques have been discussed[37] and assessed.[3] Here, we report on the simplest form of analysis, referred to as one-at-a-time sensitivity analysis[15] or *ceteris paribus* approach.[37] This involves varying input parameters independently one at a time, all other parameters being constant, and observing the resulting influence on model predictions. This form of sensitivity analysis was selected because it is easy to understand by non-experts, relatively simple to implement and because it provides a direct assessment of sensitivity without using any transformation in the relationship between model input and model output. In contrast, Monte

Carlo methods for sensitivity analysis rely on the linearisation of this relationship and this may lead to the introduction of a bias in the sensitivity assessment for highly non-linear formulations such as pesticide leaching models.[9,38] Disadvantages of the one-at-a-time approach are that (1) it is more computationally intensive than other methods when the analysis involves a large number of parameters,[3] (2) it is not suited to the study of the influence of large variations of input parameters on model predictions, and (3) it does not take into account interactions resulting from the simultaneous variation of multiple parameters.

A number of studies have focussed their sensitivity analysis on those few model input parameters which are expected to be the most influential.[39,40] Here, the number of parameters included in the analyses was maximised to ensure that sensitivity results would not reflect prior judgement on model sensitivity. In some instances, variations of a number of model input parameters were linked. This was particularly the case for parameters which varied with depth. In these instances, the variation of parameters at depth ('slave parameters') was linked to that of parameters for the topsoil ('primary parameters'). For instance, a given increase in $K_d$ values in the topsoil was supported by the same relative increase in $K_d$ values at depth. The total number of parameters (primary and slave parameters) which were varied in the sensitivity analyses was 44, 40, 142 and 99 parameters for PELMO, PRZM, PESTLA and MACRO, respectively. Parameters which were included in the sensitivity analyses are presented in Appendices 1 to 4.

In contrast to studies where model input has been varied by standard percentages regardless of the extent of the variation expected for specific model inputs,[2,26] parameters in the present study were varied within a range which reflected their uncertainty. A broad definition of uncertainty was adopted here and variation ranges not only reflected variability in the field, but also uncertainty associated with approximations and inaccuracies, eg differences in sample preparation, variability in laboratory determinations, measurement error.[41] Maximum variation ranges were assigned to input parameters by expert judgement following their discussion between the three authors. In general, parameters which are determined experimentally were varied symmetrically (ie same variation for increase and decrease of the parameter). Parameters related to sorption and degradation were considered as relatively uncertain and it was decided that a reasonable range of variation for most was obtained by multiplying and dividing the average value by a factor of two. Parameters that are not readily determined experimentally were varied according to expert judgement. Where appropriate, model developers were contacted to discuss particular parameter variations. Attention was paid to vary the parameters in the same way between models. Each input parameter was varied by a number of increments (from six to 24 depending on the input parameter considered) which were broadly proportional to the variation applied. Minimum and maximum deviations applied to parameters are presented in Appendices 1 to 4.

The outputs used to estimate the sensitivity of the four models were the cumulative percolation of water at the bottom of soil cores (known as 'recharge' in PRZM and PELMO) and the cumulative areal mass of pesticide lost via leaching (subsequently referred to as 'pesticide loss'). For PRZM, cumulative recharge was taken from the annual values for the 'leaching output' from the bottom layer of the 1-m profile (cm of water). Cumulative pesticide losses were computed from annual values for 'pesticide leached below core depth' (given in kg ha$^{-1}$). For PELMO, cumulative recharge was calculated from the annual values of 'recharge below soil core' (in cm of water) which can be found in the 'wasser.plm' output file. Similarly, cumulative pesticide losses were computed from values of 'pesticide leached below core' (given in kg ha$^{-1}$) in the 'chem.plm' output file for each year of the simulation period. For PESTLA, annual percolation was extracted from the file 'bawafc.out' (PRBT = water percolated annually through the bottom of the system, in mm). Pesticide losses were computed from the cumulative loss per area out of the bottom of the system (in kg ha$^{-1}$) from the file 'leacos1.out'. For MACRO, the binary output file produced by the model was post-processed automatically by a batch file to generate a file with the values of cumulative percolation (MACRO parameter 'TFLOWOUT') and cumulative solute leaching (MACRO parameter 'TSOUT'). The SENSAN instruction file then read the last values of the file. Cumulative solute leaching was converted from mg m$^{-2}$ to g ha$^{-1}$. Predicted percolation volumes were all converted to mm while model predictions for pesticide loss were expressed in g ha$^{-1}$.

### 2.4 Assessment of model sensitivity

The assessment of model sensitivity was based on the ratio of the relative variation in model output to the relative variation in model input. For each variation increment, the relative variation in model input and model output were calculated as follows:

$$\text{Input variation} = \frac{I - I_{BC}}{I_{BC}} * 100 \tag{1}$$

$$\text{Output variation} = \frac{O - O_{BC}}{O_{BC}} * 100 \tag{2}$$

where $I$ is the value of the input parameter, $I_{BC}$ is the value of the input parameter for the base-case scenario, $O$ is the value of the output variable, and $O_{BC}$ is the value of the output variable for the base-case scenario.

The ratio of variation (ROV) can be defined as follows:

$$\text{ROV} = \frac{\text{Output variation}}{\text{Input variation}} \tag{3}$$

Or,

$$\text{ROV} = \frac{O - O_{BC}}{I - I_{BC}} * \frac{I_{BC}}{O_{BC}} \tag{4}$$

The ratio can be either positive or negative. It takes negative values if a decrease in an input parameter results in an increase in the output value or if an increase in an input parameter results in a decrease in the output value. The sign of the ratio is not critical when the aim is to classify input parameters according to their influence on model output. Hence, the absolute value of ROV (|ROV|) was considered for classification purposes.

It was decided to represent the influence of a particular input parameter by the maximum absolute ratio of variation (MAROV),

$$\text{MAROV} = \text{Max}_i|\text{ROV}|, \quad i = 1 \text{ to } r, \tag{5}$$

where $r$ is the number of variation increments applied to a particular parameter.

The larger the MAROV index, the more influence a parameter has on model output. A MAROV of 1 means that a variation in the model input of $x$% will result at maximum in the same variation in the model output ($x$%). If MAROV equals 10, the disturbance of a model input will be propagated through the model and amplified to result in a maximum variation of the output by 10 times more.

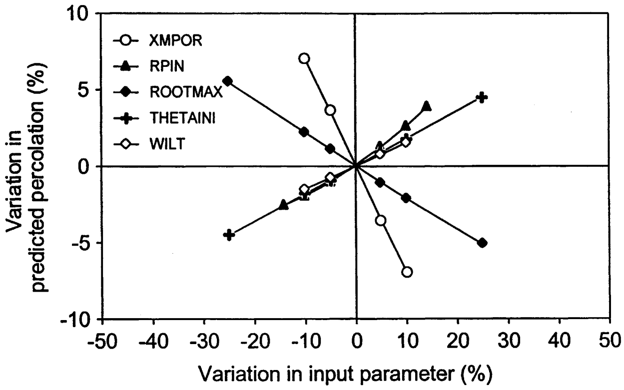


**Figure 3.** Example of chart showing the variation in MACRO predictions for percolation in response to the modification of input parameters. Only the five parameters which have the most influence on percolation predictions are presented. A brief description of the parameters can be found in Appendix 4.

The plotting of the output variation versus the input variation provides a graphical means to assess the sensitivity of the model to input parameters. An example is provided in Fig 3 which presents results

**Table 2.** Predictions for percolation and pesticide losses by the four models for the four base-case scenarios

| | Scenario | | | |
|---|---|---|---|---|
| | Wick soil | | Hodnet soil | |
| | Pesticide 1 | Pesticide 2 | Pesticide 1 | Pesticide 2 |
| PELMO | | | | |
| Total number of years run | 4 | 9 | 7 | 10 |
| Total percolation per annum (mm)[a] | 242/241 | 242/241 | 224/223 | 224/223 |
| Total pesticide loss predicted at 1-m depth ($g\ ha^{-1}$) | 25.7 | 0.23 | 0.31 | $1.11 \times 10^{-7}$ |
| Total pesticide loss predicted at 1-m depth (% of applied) | 1.29 | 0.01 | 0.02 | $5.53 \times 10^{-6}$ |
| PRZM | | | | |
| Total number of years run | 10 | 10 | 10 | 10 |
| Total percolation per annum (mm)[a] | 350/305 | 350/305 | 347/293 | 347/293 |
| Total pesticide loss predicted at 1-m depth ($g\ ha^{-1}$) | 31.7 | 0.52 | 0.89 | $4.04 \times 10^{-3}$ |
| Total pesticide loss predicted at 1-m depth (% of applied) | 1.59 | 0.03 | 0.04 | $2.02 \times 10^{-4}$ |
| PESTLA | | | | |
| Total number of years run | 8 | 8 | 8 | 8 |
| Total percolation per annum (mm)[a] | 326/326 | 326/326 | 329/329 | 329/329 |
| Total pesticide loss predicted at 1-m depth ($g\ ha^{-1}$) | 38.8 | 0.61 | 3.26 | 0.04 |
| Total pesticide loss predicted at 1-m depth (% of applied) | 1.84 | 0.03 | 0.16 | $2.10 \times 10^{-3}$ |
| MACRO | | | | |
| Total number of years run | 4 | 6 | 4 | 4 |
| Total percolation per annum (mm)[a] | 242/283 | 242/283 | 230/271 | 230/271 |
| Total pesticide loss predicted at 1-m depth ($g\ ha^{-1}$) | 33.82 | 7.52 | 39.80 | 87.29 |
| Total pesticide loss predicted at 1-m depth (% of applied) | 1.69 | 0.38 | 1.99 | 4.36 |

[a] Percolation in the first year/percolation in subsequent years.

for the five parameters which most influence MACRO predictions for percolation. The closer the curve to the Y axis (the larger the slope of the line linking the origin and a particular point), the more sensitive the model to this parameter. In the same way, the closer the curve to the X axis (the smaller the slope of the line linking the origin and a particular point), the less sensitive the model to this parameter. Curves corresponding to positive influences (an increase in model output resulting from an increase in model input or a decrease in model output resulting from a decrease in model input) are located in the top right and bottom left quadrants while those corresponding to negative influences (an increase in model output resulting from a decrease in model input or a decrease in model output resulting from an increase in model input) are situated in the top left and bottom right quadrants. The MAROV value in these plots of output variation versus input variation can be read as the maximum slope of the lines linking the origin to data points for the various increments. The use of the maximum slope might lead to a small overestimation of sensitivity in instances where there is non-linearity in the response of the model to changes in input parameters (eg RPIN in Fig 3). Parameters which mainly displayed non-linearity in their relationship to pesticide loss were those related to sorption and degradation.

## 3 RESULTS

### 3.1 Simulation of base-case scenarios by the four models

The four base-cases resulted from simulating the leaching of Pesticides 1 and 2 in the Wick and Hodnet soils. Predictions for accumulated percolation and pesticides losses for the four models are presented in Table 2. Predicted pesticide breakthrough in leachate is presented in Figs 4, 5, 6 and 7 for PELMO, PRZM, PESTLA and MACRO, respectively. Figures 4 and 5 are presented on a monthly time-step while a daily time-step was used in Figures 6 and 7. The adoption of a monthly time-step was due to practical difficulties associated with dealing with the large (>120 MB) PELMO and PRZM output files generated when these models were used for 10-year simulations on a daily time-step. Average pesticide concentrations calculated over a period of 10 years for the four base-case scenarios were in the range <0.001 to 3.2 μg litre$^{-1}$ for the four models (data not shown). Scenarios can therefore be considered broadly relevant to the pesticide registration context where a threshold concentration of 0.1 μg litre$^{-1}$ in water leaching to 1-m depth is used as a trigger for further work to investigate potential groundwater contamination in Europe.

PELMO predictions for percolation (*ca* 230 mm per year) were smaller than those by PRZM (*ca* 300 mm per year). Potential evapotranspiration data

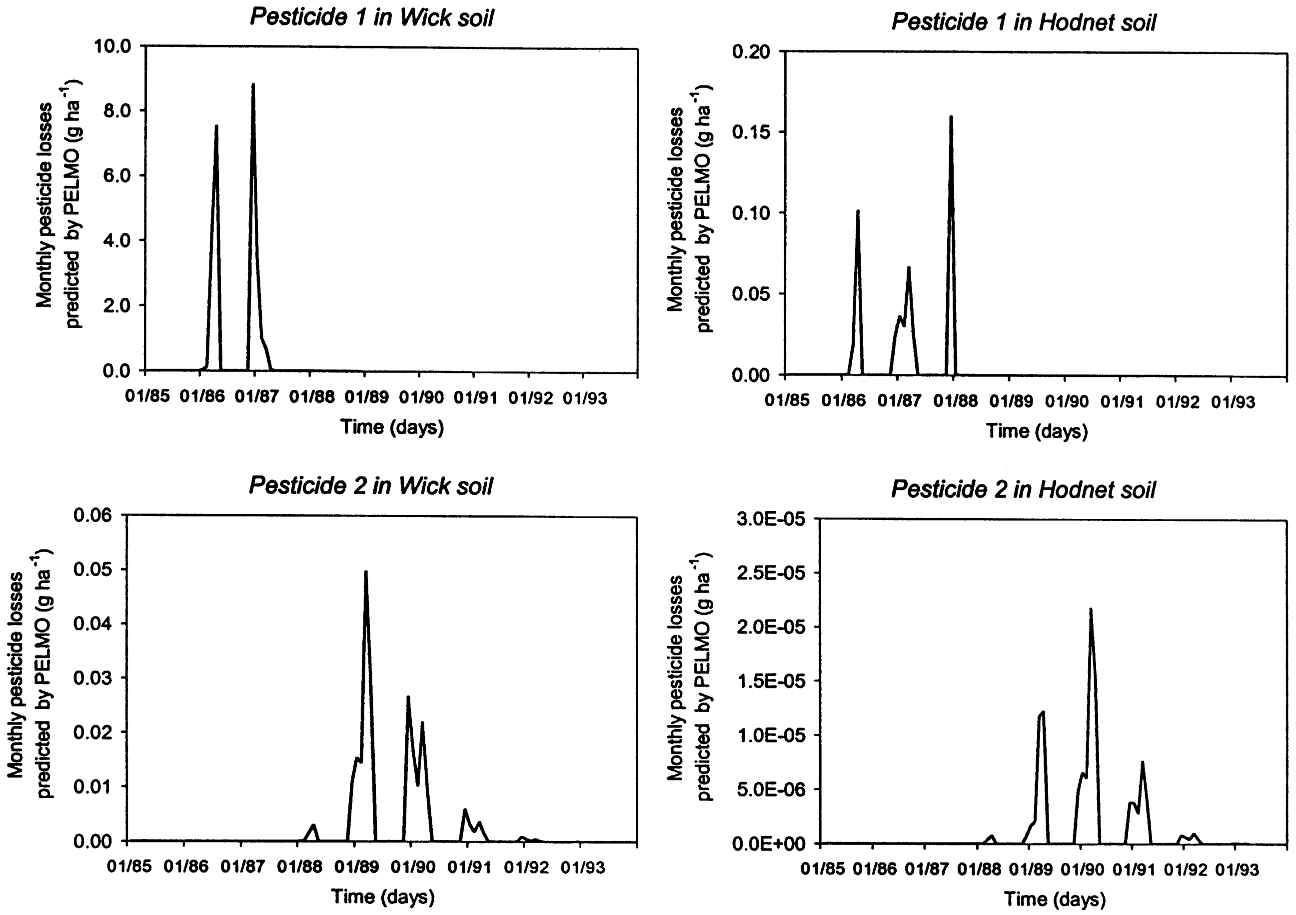


**Figure 4.** Monthly predictions for pesticide losses by PELMO for the four base-case scenarios.

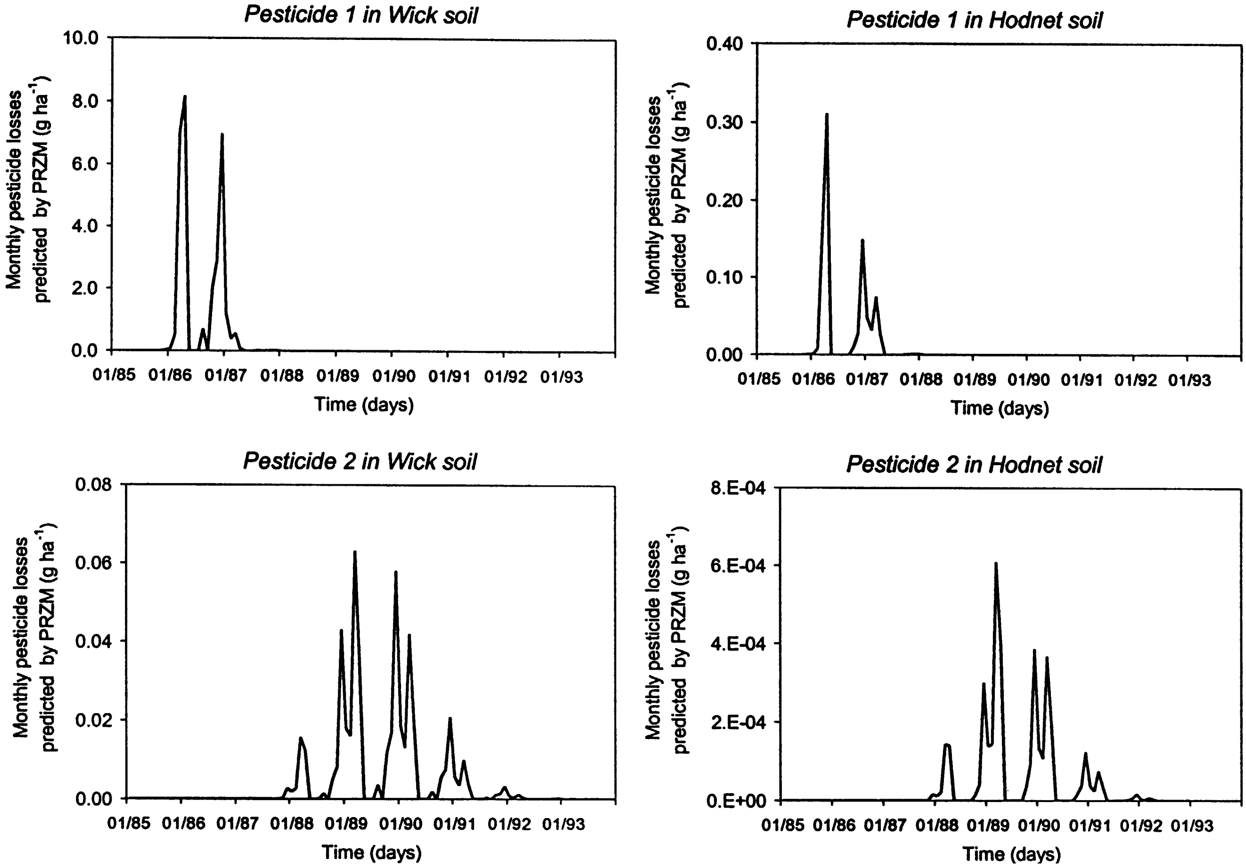


**Figure 5.** Monthly predictions for pesticide losses by PRZM for the four base-case scenarios.

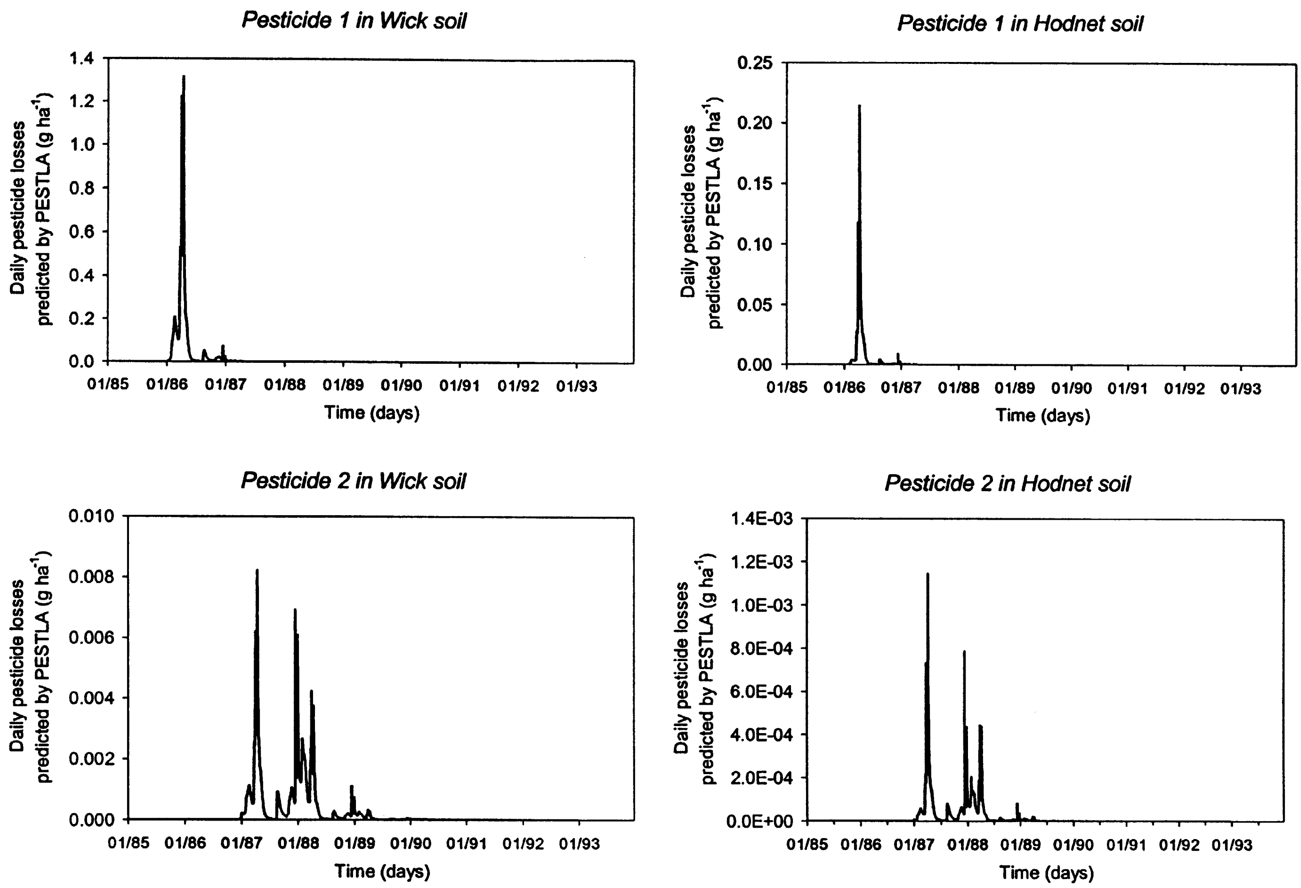


**Figure 6.** Daily predictions for pesticide losses by PESTLA for the four base-case scenarios.

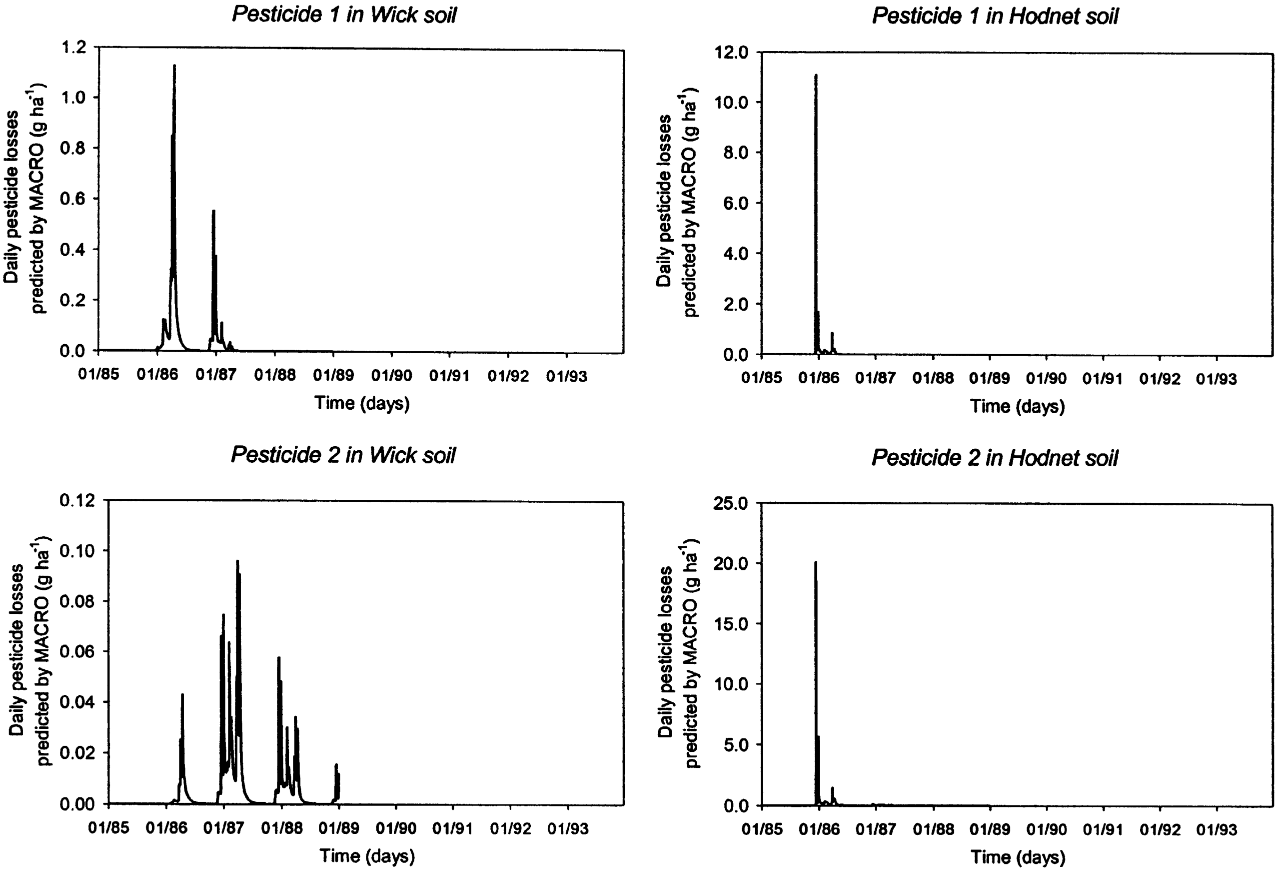


**Figure 7.** Daily predictions for pesticide losses by MACRO for the four base-case scenarios.

were supplied to the model by selecting the option 'own ET data', but it later transpired that PELMO was reading PET as actual evapotranspiration. This means that parameters related to the calculation of actual evapotranspiration from potential data (ANET, AMXD; Appendix 1) were found to have no influence on model predictions. PELMO and PRZM predictions for pesticide loss were broadly similar, reflecting the common root of these two capacity models. Pesticide loss was only predicted to occur from December to April each year for PELMO and from October to April for PRZM, in line with predicted percolation timings. Slightly larger losses were predicted by PRZM when compared to PELMO. For both models, losses were predicted to be larger for Pesticide 1 than for Pesticide 2 and for the sandy loam (Wick soil) than for the clay loam (Hodnet soil). Pesticide leaching profiles were similar for the two soils, but differed significantly between the two pesticides. Pesticide 1 was characterised by a leaching pattern which started at the end of the first year and which extended over two years, whereas leaching for Pesticide 2 was initiated at the end of the third year and lasted for longer. Full pesticide breakthrough was simulated after 3–9 years for the different scenarios and maximum monthly loadings were predicted to occur from 14–53 months and from 6 to 41 months after application for PELMO and PRZM, respectively.

The PESTLA model simulated similar volumes of water percolating through the two profiles (326 and 329 mm per year for the Wick and Hodnet soils, respectively). As for PELMO and PRZM, total pesticide losses were predicted to be largest for the scenario involving Pesticide 1 in the Wick soil and predictions were much smaller for the three remaining scenarios. Losses were predicted to be larger for Pesticide 1 than for Pesticide 2 and for the sandy loam than for the more structured clay loam. Leaching breakthrough was dependent on the compound considered. Losses of Pesticide 1 by percolation occurred over a period of one year and were dominated by a single leaching event occurring in mid-April, whereas losses were simulated over 3–4 years for Pesticide 2 and were more evenly distributed between the years. Although larger pesticide losses were predicted by PESTLA when compared to PRZM and PELMO, especially for the more structured Hodnet soil, the three models showed a similar behaviour overall.

In contrast to other models, MACRO predicted losses for both pesticides which were larger in the clay loam (Hodnet) than in the sandy loam (Wick), especially for Pesticide 2. This reflects greater leaching by preferential flow in the more highly structured Hodnet soil. Pesticide dissolved in water moving rapidly through the soil profile via macropores may be subject to less sorption and degradation in the more reactive upper part of the profile. Losses of Pesticide 1 were predicted to be larger than those of Pesticide 2 in the Wick soil, but the reverse was predicted in the Hodnet soil. This highlights the complex interactions between compounds and the soil environment and, again, the influence of considering preferential flow processes in the modelling. Leaching breakthrough was most dependent on soil type rather than compound. In the sandy loam Wick soil, losses by percolation occurred over relatively long time periods (eg over 7.5 and 5 months per year for Pesticide 1 in the Wick soil) and total leaching occurred over 2 and 4 years for Pesticide 1 and 2, respectively. In contrast, pesticide losses from the more structured Hodnet soil were short-lived and dominated by transient peaks in a single year with much larger daily losses. Maximum daily losses were 10 and 209 times larger in the clay loam than in the sandy loam for Pesticide 1 and 2, respectively.

### 3.2 Sensitivity of PELMO

Parameters which were found to influence prediction of percolation by PELMO are presented in Table 3. Results from sensitivity analyses with regard to the prediction of water percolation by PELMO

**Table 3.** MAROV values for model parameters with the largest influence on predictions for percolation. Parameters are presented by decreasing order of influence (1 = most influential parameter). Only those parameters which were found to influence percolation are included. A brief description of parameters can be found in Appendices 1 to 4

| | Scenario | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Wick soil | | | | Hodnet soil | | | |
| Ranking | Pesticide 1 | | Pesticide 2 | | Pesticide 1 | | Pesticide 2 | |
| PELMO | | | | | | | | |
| 1 | WC-FC | 0.648 | WC-FC | 0.641 | WC-FC | 1.2 | WC-FC | 1.2 |
| 2 | WP | 0.208 | WP | 0.208 | WP | 0.519 | WP | 0.519 |
| 3 | CINT | 0.003 | CINT | 0.004 | CINT | 0.019 | CINT | 0.020 |
| 4 | COVM | 0.003 | COVM | 0.004 | COVM | 0.019 | COVM | 0.020 |
| PRZM | | | | | | | | |
| 1 | FC | 0.457 | FC | 0.457 | FC | 0.613 | FC | 0.613 |
| 2 | ANET | 0.262 | ANET | 0.262 | WP | 0.324 | WP | 0.324 |
| 3 | AMXD | 0.210 | AMXD | 0.210 | ANET | 0.290 | ANET | 0.290 |
| 4 | WP | 0.169 | WP | 0.169 | AMXD | 0.235 | AMXD | 0.235 |
| 5 | CINT | 0.015 | CINT | 0.015 | CINT | 0.015 | CINT | 0.015 |
| 6 | COVM | 0.015 | COVM | 0.015 | COVM | 0.015 | COVM | 0.015 |
| PESTLA | | | | | | | | |
| 1 | CFTB | 0.331 | CFTB | 0.331 | CFTB | 0.332 | CFTB | 0.332 |
| 2 | COFR | 0.307 | COFR | 0.307 | COFR | 0.304 | COFR | 0.304 |
| 3 | G6 | 0.153 | G6 | 0.153 | G6 | 0.243 | G6 | 0.243 |
| 4 | G2 | 0.153 | G2 | 0.153 | RSIG | 0.134 | RSIG | 0.134 |
| 5 | RDTB | 0.153 | RDTB | 0.153 | IF1 | 0.061 | IF1 | 0.061 |
| 6 | RSIG | 0.123 | RSIG | 0.123 | IR1 | 0.061 | IR1 | 0.061 |
| 7 | IF1 | 0.115 | IF1 | 0.115 | GCTB | 0.03 | GCTB | 0.03 |
| 8 | IR1 | 0.115 | IR1 | 0.115 | G4 | 0.015 | G4 | 0.015 |
| 9 | GCTB | 0.061 | GCTB | 0.061 | G3 | 0.004 | G3 | 0.004 |
| 10 | RDS | 0.061 | RDS | 0.061 | G2 | 0 | G2 | 0 |
| 11 | G1 | 0.038 | G1 | 0.038 | RDTB | 0 | RDTB | 0 |
| 12 | G3 | 0.031 | G3 | 0.031 | RDS | 0 | RDS | 0 |
| MACRO[a] | | | | | | | | |
| 1 | XMPOR | 0.728 | XMPOR | 0.728 | XMPOR | 0.856 | XMPOR | 0.856 |
| 2 | RPIN | 0.274 | RPIN | 0.274 | RPIN | 0.371 | RPIN | 0.371 |
| 3 | ROOTMAX | 0.226 | ROOTMAX | 0.226 | THETAINI | 0.320 | THETAINI | 0.320 |
| 4 | THETAINI | 0.181 | THETAINI | 0.181 | WILT | 0.300 | WILT | 0.300 |
| 5 | WILT | 0.153 | WILT | 0.153 | ROOTMAX | 0.280 | ROOTMAX | 0.280 |
| 6 | ZALP | 0.122 | ZALP | 0.122 | TPORV | 0.236 | TPORV | 0.236 |
| 7 | ZLAMB | 0.114 | ZLAMB | 0.114 | ZALP | 0.133 | ZALP | 0.133 |
| 8 | CTEN | 0.113 | CTEN | 0.113 | CTEN | 0.095 | CTEN | 0.095 |
| 9 | KSM | 0.042 | BETA | 0.042 | ZLAMB | 0.054 | ZLAMB | 0.054 |
| 10 | TPORV | 0.034 | KSM | 0.034 | BETA | 0.054 | BETA | 0.054 |
| 11 | BETA | 0.033 | GAMMA | 0.033 | ZN | 0.049 | ZN | 0.049 |
| 12 | ZN | 0.014 | TPORV | 0.014 | GAMMA | 0.021 | GAMMA | 0.021 |
| 13 | WATEN | 0.013 | WATEN | 0.013 | LAIMAX | 0.018 | LAIMAX | 0.018 |
| 14 | GAMMA | 0.012 | ZN | 0.012 | KSATMIN | 0.015 | KSATMIN | 0.015 |
| 15 | LAIMAX | 0.011 | LAIMAX | 0.011 | RINTEN | 0.007 | RINTEN | 0.007 |

[a] Only the 15 most influential parameters are presented.

were dependent on the soil considered. Recharge volumes predicted by PELMO were only slightly affected by changes in input parameters (maximum MAROV values 0.65 and 1.17 for the Wick and Hodnet soil, respectively) with the most sensitive parameters those related to the soil water content (ie field capacity, initial soil moisture content at the start of the simulation and wilting point) for all scenarios. Crop-related parameters which were considered in this study (maximum interception storage and maximum soil cover) had little effect on predicted volumes of recharge. The sensitivity of recharge was approximately twice as large for the Hodnet scenarios compared to the Wick scenarios.

In contrast to recharge, the prediction of pesticide losses was very sensitive to some parameters (MAROV > 10; Fig 8). The maximum MAROV value was >10 000 for the scenario involving Pesticide 2 and the Hodnet soil. Such large sensitivities may be artefacts resulting from the small pesticide loss predicted for this particular scenario and the use of the maximum slope in the definition of MAROV. However, whilst absolute MAROV values for this specific scenario may be discarded, results for parameter ranking according to their sensitivity remain valid. Sensitivity of PELMO may be related to some extent to the amount of pesticide loss that was predicted (the greater the loss, the less sensitive the model), although this was only verified within soil types in this study. Figure 8 presents the PELMO parameters ranked by their influence on pesticide losses for the four scenarios. The top six most sensitive parameters were identical for the four scenarios, although the detailed ranking of these parameters changed according to the scenario considered. These included all parameters related to degradation (degradation rates DEGR, the factor of increase in degradation when temperature is increased by 10 °C QTEN, the soil moisture for the incubation during degradation studies ASM, and the exponent of the equation describing the influence of moisture on degradation MEXP), the two parameters related to sorption (the Freundlich exponent NF and the Freundlich coefficient KF) and two soil parameters (the field capacity/initial soil moisture content WC/FC and the bulk density BUD). Degradation rates were found to be the most influential parameters for the prediction of pesticide loss in three of the four scenarios.

### 3.3 Sensitivity of PRZM

For both soils, percolation volumes predicted by PRZM were only sensitive to a few parameters. The magnitude of the change in predicted recharge when input parameters were varied was rather

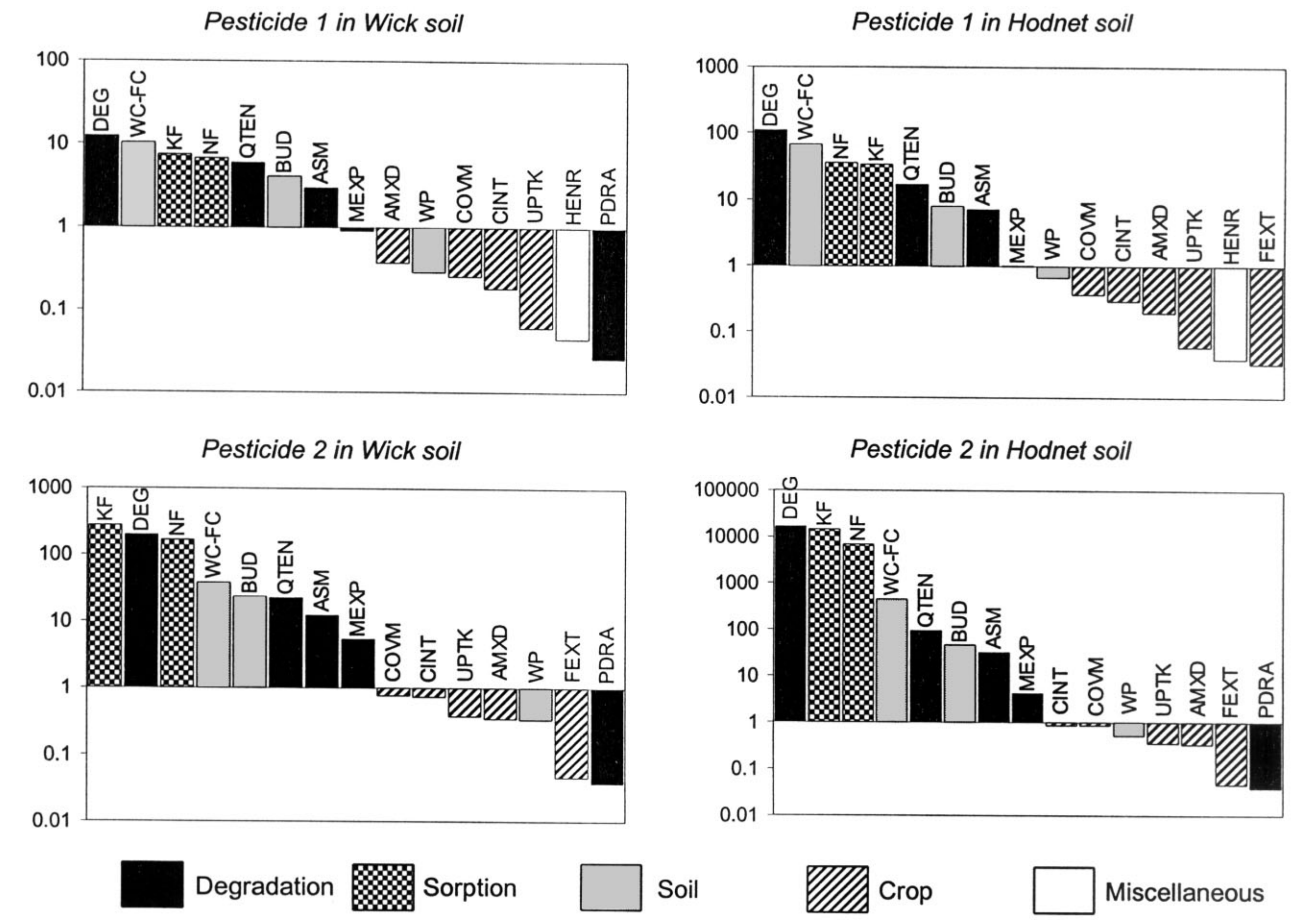


**Figure 8.** Sensitivity results for PELMO to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 1.

small (MAROV < 0.7) and it was only marginally affected by the nature of the soil. The PRZM input parameter which had the most influence on predictions was 'field capacity', which in the present study combined the field capacity value as determined from the water release curve and the soil moisture content at the beginning of the simulations (initial soil moisture contents in the model were set at field capacity). Parameters which were found to influence the prediction of recharge were those related to the moisture status of the soil (field capacity, wilting point), to the computation of actual evapotranspiration from potential evapotranspiration data (minimum depth for extraction of evaporation) and to the description of the plant cover (maximum rooting depth, maximum interception storage and maximum areal coverage of the canopy).

In contrast, prediction of losses of pesticides by PRZM were very much affected by changes in input parameters. The magnitude of the sensitivities varied for the different scenarios (Fig 9). Large sensitivities were found for all four scenarios (maximum MAROV value *ca* 3500) and the largest sensitivities were associated with Pesticide 2 which was predicted to leach to only a small extent in both soils. In the fourth scenario involving Pesticide 2 in the Hodnet soil, an increase by 10% of the Freundlich exponent from 0.9 to 0.99 was found to increase total pesticide losses from 0.004 to 0.37 g ha$^{-1}$. The same increase in the Freundlich exponent for the scenario involving Pesticide 1 and the Wick soil resulted in a smaller increase in pesticide losses from 31.7 g ha$^{-1}$ to 47.6 g ha$^{-1}$. Figure 9 presents the 15 parameters which were found to most influence predictions of total pesticide losses by PRZM. Although the most influential parameters and the detailed ranking differed for each scenario, the same parameters were consistently found at the top of the list. This was particularly obvious for the first six parameters which were related to pesticide sorption (Freundlich distribution coefficients and exponent), pesticide degradation (degradation rates, QTEN) as well as the description of the soil (field capacity/initial soil moisture content, bulk density). As for PELMO, field capacity appeared as one of the most influential parameters for the predictions of pesticide losses by PRZM (see for instance the scenario involving Pesticide 1 in the Wick soil). No clear relationship could be derived between sensitivity rankings and pesticide or soil types. Significant similarities were observed in the results for PRZM and PELMO.

### 3.4 Sensitivity of PESTLA

Results from the sensitivity analysis for the prediction of percolation by PESTLA are presented in

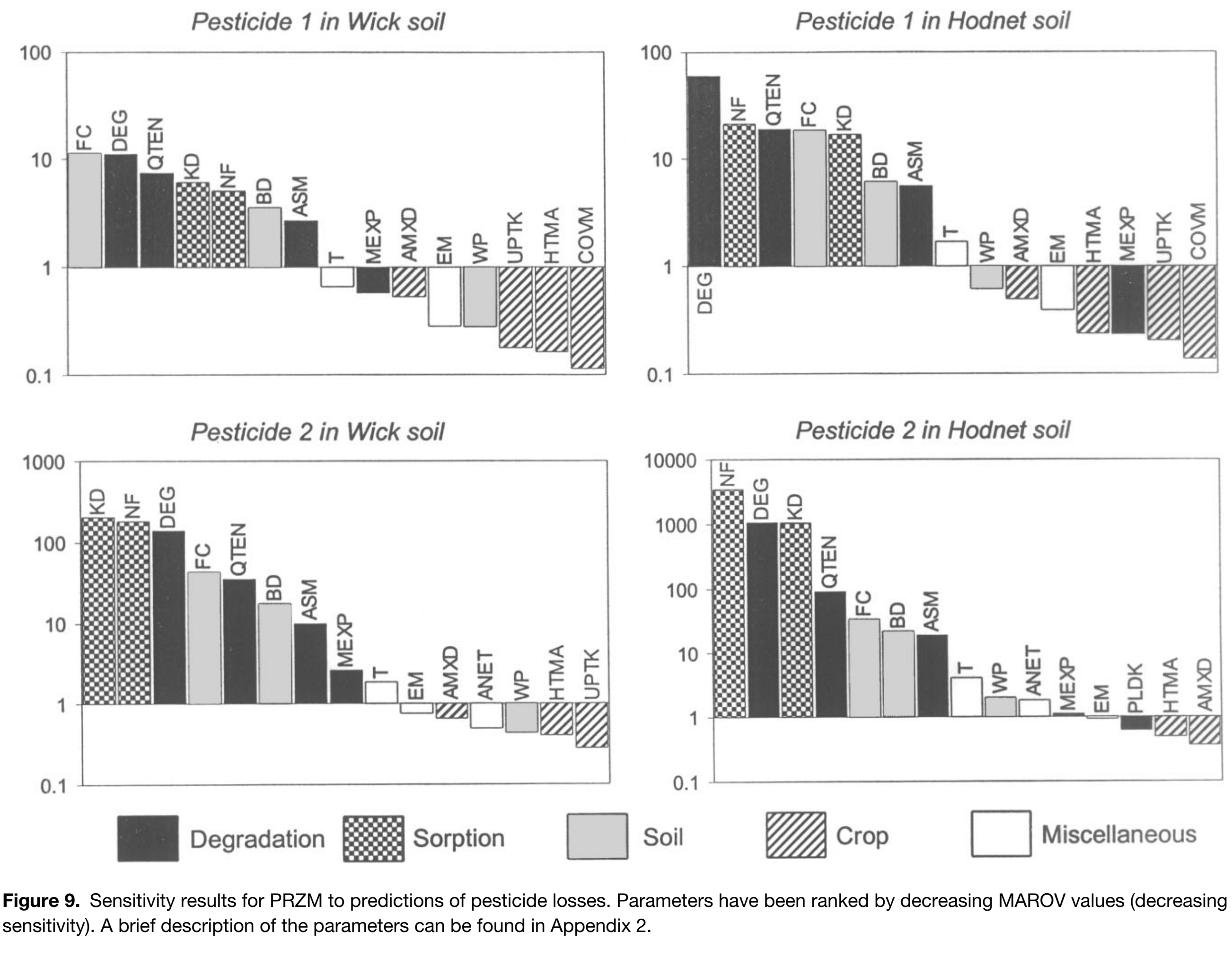


**Figure 9.** Sensitivity results for PRZM to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 2.

Table 3. A large number of input parameters affected percolation predicted by PESTLA (12 parameters for the Wick soil, nine parameters for the Hodnet soil), but their influence was rather small (MAROV values < 0.35). Influential parameters included crop variables (crop factor, extinction coefficients, maximum rooting depth, maximum leaf area index, maximum rooting depth allowed by the soil profile), those related to evapotranspiration (soil evaporation coefficient, minimum rainfall to reset models used in the computation of actual from potential evapotranspiration) and those related to the description of the water release characteristics (parameters of the Van Genuchten equation).[42]

PESTLA predictions for pesticide losses were greatly affected by changes in input parameters (Fig 10). The magnitude of the sensitivities was dependent on the different scenarios and was smallest for the scenario where the greatest losses were predicted (Pesticide 1 on Wick, maximum MAROV 5.9) and greatest for the scenario where the smallest losses were predicted (Pesticide 2 on Hodnet, maximum MAROV value *ca* 360). In the scenario involving Pesticide 2 in the Hodnet soil, a modification of the Freundlich exponent from 0.9 to 0.99 resulted in an increase of pesticide losses from 0.043 g ha$^{-1}$ to 0.864 g ha$^{-1}$. There was a relative consistency in the ranking for the most sensitive parameters, except for the scenario involving Pesticide 1 in the Hodnet soil. The most sensitive parameters were generally those related to sorption (Freundlich coefficient and exponent) and degradation (half-life, molar activation energy of degradation). The organic matter content was also found to have a relatively large influence on predicted pesticide losses. In contrast to other models, the description of sorption used in PESTLA for the four scenarios made use of $K_{om}$ and the organic matter content. In the third scenario involving Pesticide 1 in the Hodnet soil, the second most sensitive parameter was the dimensionless exponent $n$ of the equation from Van Genuchten which describes the water retention curve. Although the bulk density did not have any influence on the prediction of percolation volumes, it had a notable influence (MAROV > 1) on the prediction of pesticide losses for all scenarios. The bulk density is used in calculating the repartition of pesticide between the solid and liquid phase.

### 3.5 Sensitivity of MACRO

Sensitivity results for MACRO have been presented in detail elsewhere[9] and only the essence of the findings for the dual-porosity model is presented below. The sensitivity of MACRO predictions for percolation to changes in input parameters is presented in Table 3. No notable difference was found in the ranking of parameters between the four scenarios. The parameter

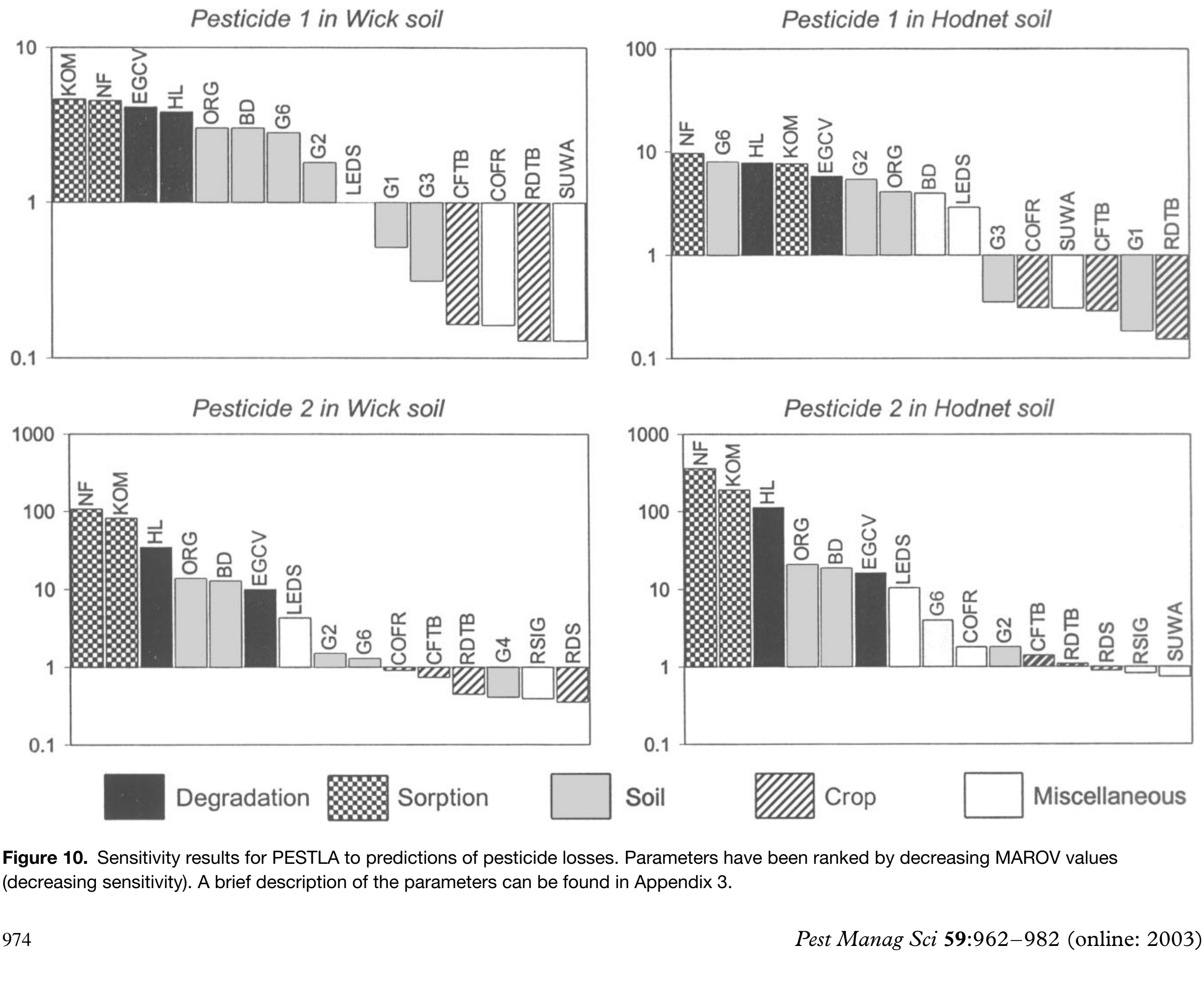


**Figure 10.** Sensitivity results for PESTLA to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 3.

which had the most influence on percolation volumes was XMPOR, the boundary soil water content. This parameter is one of three (CTEN, XMPOR and KSM) which define the boundary between micropores and macropores in MACRO. Other parameters related to the description of soil water content and water retention (THETAINI, WILT and TPORV) were found to have some influence on percolation results. The influence of the initial soil moisture content (THETAINI) emphasises that a pre-run of a few months or years should be carried out to allow equilibration of the model with respect to water content in the soil profile.

The 15 parameters which showed the largest influence on the predictions of pesticide losses by MACRO are presented in Fig 11. In the Wick soil, which is coarser textured and more weakly structured than the Hodnet soil, MACRO was most sensitive to three parameters related to the degradation (degradation rates) or sorption of pesticides (Freundlich coefficient and exponent). Following these three dominant parameters (and TRESP, the parameter which describes the influence of temperature on degradation kinetics, for the first scenario), the next most influential inputs were related to the description of the soil hydrology and the soil (XMPOR, ZN, GAMMA). In the Hodnet soil, pesticide losses simulated by the MACRO model were much more influenced by hydrological parameters. TPORV (the water content at saturation) was the most and second most influential parameter for the Hodnet scenarios involving Pesticide 2 and 1, respectively. In the scenario with Pesticide 2, five out of the six top parameters were hydrological parameters. The second most influential parameter for the scenario involving Pesticide 2 and the Hodnet soil (ZN, pore size distribution index) is particularly uncertain because it is difficult to determine experimentally and little guidance is available. Although the sorption coefficient (ZKD in Fig 11) was found to greatly influence results for pesticide losses in the Wick soil (ranked 2 and 3), its influence was much less pronounced in the Hodnet soil (ranked 10 and 16).

## 4 DISCUSSION

The leaching of two pesticides in two contrasting soil types was simulated using the four main models which have been used for pesticide registration in Europe in the last decade. The aim of model parameterisation within the scope of the present exercise was not to attempt to provide a good match between predictions of the different models, ie no model benchmarking was undertaken. Although differences between leaching models used for pesticide registration have lessened in the last decade, they still present their individualities[43]

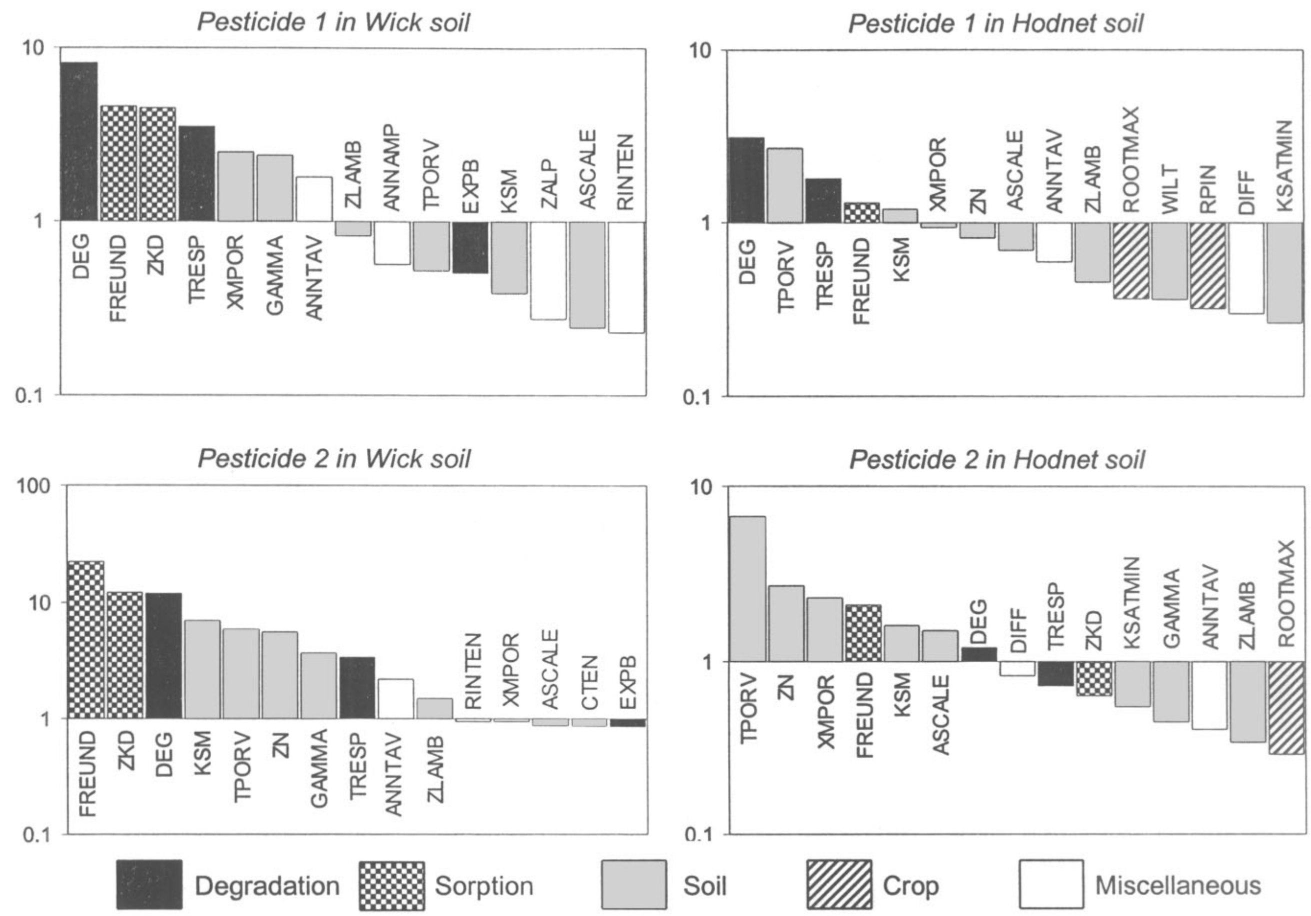


**Figure 11.** Sensitivity results for MACRO to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 4.

and this will lead to differences in predictions.[11] Present results for the prediction of pesticide loss suggest that the estimation of the leaching potential of a compound will be significantly influenced by the model used. Model selection is therefore likely to be a significant source of uncertainty in pesticide fate modelling. A possible way to account for this uncertainty would be to predict pesticide leaching using a range of models. Predictions for pesticide losses by PELMO, PRZM and PESTLA were generally found to be within a factor of $<3$ for the sandy loam. In contrast, little leaching was predicted in the clay loam by the three models and differences of several orders of magnitude were noted. The preferential flow model MACRO contrasted with the three chromatographic flow models, especially for the finer-textured soil where a different leaching pattern and greater loss than in the sandy loam was predicted.

Both the magnitude of the sensitivity and the detailed ranking of parameters according to their influence on model predictions were found to be dependent on the scenario considered. This confirms the importance of using multiple base-case scenarios, but also suggests that sensitivity results presented here should not be used regardless of the modelling situation at hand. In those instances where the modelling differs significantly from that presented here (eg different model output considered, different main dissipation processes), it is suggested that a limited sensitivity analysis is carried out.

Although the number of model input parameters which were varied in the present sensitivity analyses was large, a number of specific parameters which can be expected to have a strong influence on model predictions were left out. For instance, the organic carbon content was not specified for three of the four models because $K_d$ values were directly fed into input files. Organic carbon content has a direct influence on the calculation of $K_d$ values when these latter values are calculated from partition coefficients normalised to organic carbon ($K_{oc}$) or organic matter ($K_{om}$). It is therefore expected that the organic carbon content will have a significant influence on model predictions for pesticide leaching.[14] Similarly, neither the influence of the pesticide application rate nor that of interception of the spraying solution by the crop were analysed. Since model runs and the processing of model output were automated to a large extent, the variation of 'switch' parameters controlling the use of subroutines was not considered. Also, the present results did not account for less obvious sensitivities such as the influence of horizon thickness on model predictions.[44]

Model predictions for percolation were found to be only slightly affected by variation in input parameters included in the present study. No meteorological data were included in the sensitivity analysis and these parameters were considered as certain. However, there is evidence of large measurement errors in meteorological datasets.[45] Potential evapotranspiration is particularly uncertain because different values are produced by different estimation methods. Given the magnitude of MAROV values that was found for percolation, the balance between PET and rainfall is expected to have by far the greatest influence on percolation predictions.

In most instances, parameters which had the largest influence on model predictions for pesticide loss were those related to sorption and degradation and these results are in line with earlier findings.[7,14,20,46] Sorption (Freundlich distribution coefficient and exponent) and degradation ($DT_{50}$) parameters are traditionally determined in the laboratory and the applicability of these values to simulate field behaviour is subject to much debate.[47] The field environment being inherently variable in space and time, half-lives and sorption coefficients should be considered as variable and uncertain.[48,49] Given the strong influence these parameters have on predictions for pesticide loss, this will transpose into uncertainty in model predictions. Uncertainty in the modelling is not limited to that in these few input parameters and may originate from a wide range of sources.[41] Predictions from pesticide leaching models should therefore be considered largely uncertain and it is desirable that this uncertainty is accounted for in risk assessment procedures for pesticides.

The exponent of the Freundlich equation which is used to describe non-linear sorption was found to be one of the most influential parameters for all models. The importance of the Freundlich exponent has been highlighted before.[38] Its influence on predictions for pesticide loss tends to increase with the strength of sorption.[7] Registration procedures for pesticides in the USA and in Europe has tended to focus on sorption distribution coefficients and degradation values as surrogates for estimating potential transfer in the environment and the importance of the Freundlich exponent has frequently been overlooked. The practical implications of current practice such as averaging parameters of the non-linear Freundlich equation for different soils[50] should be investigated and the Freundlich exponent should be considered as important as $K_{oc}$ (or $K_{om}$) when estimating pesticide leaching at low levels.[7]

A large effect of hydrological parameters on prediction for pesticide loss was noted in a number of scenarios for each of the four models used here. Such comparatively large influences of hydrological parameters have rarely been reported,[26] but can be expected since water fluxes remain a governing process for the leaching of solutes to groundwater.[10] Field capacity and bulk density values were found to significantly influence pesticide loss for the capacity models PRZM and PELMO. This implies that field capacity needs to be determined with care[26] and uncertainty in this variable should be minimised as far as possible. Both analytical procedures for establishing water retention curves and the practical definition of field capacity differ between countries. Field capacity is normally estimated as the soil water content at a particular water tension from the water retention curve, but there is no international agreement as to what this tension should be. A value of *ca* −33 kPa is used in the USA and Germany whilst other values are used elsewhere (eg −5 kPa in the UK, −10 kPa in The Netherlands). Guidance on the selection of field capacity values has recently been provided by FOCUS[31] and will help to reduce this source of uncertainty in the modelling.

Sensitivity results for the two capacity models PRZM and PELMO were broadly similar, in accordance with their common root in development. The number of parameters showing a large influence on predictions for pesticide loss for these two models was small compared to PESTLA and MACRO, but the magnitude of sensitivity exceeded that of the two models with a more complex description of hydrology for all four scenarios. A common preconception is that Richards' equation models, and in particular MACRO,[51] are more difficult to parameterise than capacity models and therefore carry a larger uncertainty in model predictions. Results presented here suggest that this is unlikely to be the case and that levels of predictive uncertainty in the prediction of pesticide leaching might be similar for the four models or even larger for the capacity models.

Probabilistic modelling and automatic calibration of models are likely to play an increasing role in environmental risk assessment for pesticides and it is important that these activities concentrate on those parameters which have the largest influence on model predictions. The data presented offer a starting point for this process for the four main models which have been used to predict pesticide leaching in Europe in the last decade.

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## APPENDIX 1
## PELMO input parameters considered in the sensitivity analysis and variation ranges applied

| Parameter | Description | Wick soil Nominal value | Wick soil Minimum value | Wick soil Maximum value | Hodnet soil Nominal value | Hodnet soil Minimum value | Hodnet soil Maximum value |
|---|---|---|---|---|---|---|---|
| *Parameterisation common to Pesticides 1 and 2* | | | | | | | |
| AMXD | Maximum active rooting depth (cm) | 60 | 30 | 100 | 60 | 30 | 100 |
| ANET | Depth of evapotranspiration computation (cm) | 15 | 5 | 25 | 15 | 5 | 25 |
| ASM | Soil moisture during degradation (–) | 0.277 | 0.208 | 0.347 | 0.349 | 0.262 | 0.436 |
| BUD[a] | Bulk density (g cm$^{-3}$) | 1.35 | 1.21 | 1.48 | 1.39 | 1.25 | 1.53 |
| CINT | Maximum interception storage (cm) | 0.15 | 0.10 | 0.30 | 0.15 | 0.10 | 0.30 |
| COVM | Maximum soil cover (%) | 90 | 80 | 100 | 90 | 80 | 100 |
| FEXT | Foliar extraction coefficient (cm$^{-1}$) | 0.10 | 0.05 | 0.15 | 0.10 | 0.05 | 0.15 |
| MEXP | Exponent for moisture correction (–) | 0.70 | 0.42 | 0.98 | 0.70 | 0.42 | 0.98 |
| QTEN | Increase in degradation given a temperature increase of 10 °C (–) | 2.20 | 1.82 | 2.72 | 2.20 | 1.82 | 2.72 |
| UPTK | Plant uptake efficiency factor (–) | 0.5 | 0 | 1 | 0.5 | 0 | 1 |
| WC-FC[a] | Water capacity, field capacity (–) | 0.277 | 0.208 | 0.347 | 0.349 | 0.262 | 0.436 |
| WP[a] | Wilting point (%vol) | 0.105 | 0.079 | 0.132 | 0.168 | 0.126 | 0.210 |
| *Parameterisation specific to Pesticide 1* | | | | | | | |
| DEGR[a] | Degradation rate (day$^{-1}$) | 0.0893 | 0.0446 | 0.1786 | 0.0893 | 0.0446 | 0.1786 |
| KF[a] | Freundlich sorption coefficient (ml g$^{-1}$) | 0.340 | 0.170 | 0.680 | 0.230 | 0.115 | 0.460 |
| NF[a] | Freundlich exponent (–) | 0.90 | 0.72 | 1.08 | 0.90 | 0.72 | 1.08 |
| PDRA | Plant decay rate (day$^{-1}$) | 0.0893 | 0.0446 | 0.1786 | 0.0893 | 0.0446 | 0.1786 |
| *Parameterisation specific to Pesticide 2* | | | | | | | |
| DEGR[a] | Degradation rate (day$^{-1}$) | 0.0298 | 0.0149 | 0.0596 | 0.0298 | 0.0149 | 0.0596 |
| KF[a] | Freundlich sorption coefficient (ml g$^{-1}$) | 1.700 | 0.850 | 3.400 | 1.150 | 0.575 | 2.300 |
| NF[a] | Freundlich exponent (–) | 0.90 | 0.72 | 1.08 | 0.90 | 0.72 | 1.08 |
| PDRA | Plant decay rate (day$^{-1}$) | 0.0298 | 0.0149 | 0.0596 | 0.0298 | 0.0149 | 0.0596 |

[a] Primary parameter to which slave parameters were linked.

## APPENDIX 2
## PRZM input parameters considered in the sensitivity analysis and variation ranges applied

| Parameter | Description | Wick soil Nominal value | Wick soil Minimum value | Wick soil Maximum value | Hodnet soil Nominal value | Hodnet soil Minimum value | Hodnet soil Maximum value |
|---|---|---|---|---|---|---|---|
| *Parameterisation common to Pesticides 1 and 2* | | | | | | | |
| A | Albedo (–) | 0.18 | 0.12 | 0.24 | 0.18 | 0.12 | 0.24 |
| AMXD | Maximum rooting depth (cm) | 60 | 30 | 100 | 60 | 30 | 100 |
| ANET | Minimum depth for extraction of evaporation (cm) | 15 | 5 | 25 | 15 | 5 | 25 |
| ASM | Reference moisture for degradation (%vol) | 0.277 | 0.208 | 0.347 | 0.349 | 0.262 | 0.436 |
| BD | Bulk density (g cm$^{-3}$) | 1.35 | 1.21 | 1.48 | 1.39 | 1.25 | 1.53 |
| CINT | Maximum interception storage (cm) | 0.15 | 0.10 | 0.30 | 0.15 | 0.10 | 0.30 |
| COVM | Maximum areal coverage of canopy (%) | 90 | 80 | 100 | 90 | 80 | 100 |
| EM | Emmissivity (–) | 0.96 | 0.94 | 0.98 | 0.96 | 0.94 | 0.98 |
| FC[a] | Field capacity (%vol) | 0.277 | 0.208 | 0.347 | 0.349 | 0.262 | 0.436 |
| FEXT | Foliar extraction coefficient (cm$^{-1}$) | 0.10 | 0.05 | 0.15 | 0.10 | 0.05 | 0.15 |

(*continued overleaf*)

Continued

| Parameter | Description | Wick soil Nominal value | Wick soil Minimum value | Wick soil Maximum value | Hodnet soil Nominal value | Hodnet soil Minimum value | Hodnet soil Maximum value |
|---|---|---|---|---|---|---|---|
| HTMA | Maximum canopy height (cm) | 55 | 45 | 65 | 55 | 45 | 65 |
| MEXP | Moisture exponent for degradation (–) | 0.70 | 0.42 | 0.98 | 0.70 | 0.42 | 0.98 |
| QTEN | QTEN (–) | 2.20 | 1.82 | 2.72 | 2.20 | 1.82 | 2.72 |
| T | Average monthly temperature at bottom boundary (°C) | 8 | 6 | 10 | 8 | 6 | 10 |
| TINI | Initial temperature of the horizon (°C) | 8 | 6 | 10 | 8 | 6 | 10 |
| UPTK | Plant uptake factor (–) | 0.5 | 0 | 1 | 0.5 | 0 | 1 |
| WP[a] | Wilting point (%vol) | 0.105 | 0.079 | 0.132 | 0.168 | 0.126 | 0.210 |
| *Parameterisation specific to Pesticide 1* | | | | | | | |
| DEG[a] | Degradation rate ($day^{-1}$) | 0.0893 | 0.0446 | 0.1786 | 0.0893 | 0.0446 | 0.1786 |
| KD[a] | Freundlich coefficient ($ml\,g^{-1}$) | 0.340 | 0.170 | 0.680 | 0.230 | 0.115 | 0.460 |
| NF | Freundlich exponent (–) | 0.90 | 0.72 | 1.08 | 0.90 | 0.72 | 1.08 |
| PLDK | Pesticide decay rate on canopy ($day^{-1}$) | 0.0893 | 0.0446 | 0.1786 | 0.0893 | 0.0446 | 0.1786 |
| *Parameterisation specific to Pesticide 2* | | | | | | | |
| DEG | Degradation rate ($day^{-1}$) | 0.0298 | 0.0149 | 0.0596 | 0.0298 | 0.0149 | 0.0596 |
| KD | Freundlich coefficient ($ml\,g^{-1}$) | 1.700 | 0.850 | 3.400 | 1.150 | 0.575 | 2.300 |
| NF | Freundlich exponent (–) | 0.90 | 0.72 | 1.08 | 0.90 | 0.72 | 1.08 |
| PLDK | Pesticide decay rate on canopy ($day^{-1}$) | 0.0298 | 0.0149 | 0.0596 | 0.0298 | 0.0149 | 0.0596 |

[a] Primary parameter to which slave parameters were linked.

## APPENDIX 3
## PESTLA input parameters considered in the sensitivity analysis and variation ranges applied

| Parameter | Description | Wick soil Nominal value | Wick soil Minimum value | Wick soil Maximum value | Hodnet soil Nominal value | Hodnet soil Minimum value | Hodnet soil Maximum value |
|---|---|---|---|---|---|---|---|
| *Parameterisation common to Pesticides 1 and 2* | | | | | | | |
| BD[a] | Bulk density ($g\,cm^{-3}$) | 1.35 | 1.21 | 1.48 | 1.39 | 1.25 | 1.53 |
| CFLI | Coefficient describing the relationship between the conversion rate and the volume fraction of liquid (–) | 0.70 | 0.42 | 0.98 | 0.70 | 0.42 | 0.98 |
| CFTB | Crop factor (–) | 0.75 | 0.50 | 1.0 | 0.75 | 0.50 | 1.0 |
| CFUP | Coefficient of uptake by plants (–) | 0.5 | 0.0 | 1.0 | 0.5 | 0.0 | 1.0 |
| COFR | Soil evaporation coefficient of Black ($cm\,day^{-1/2}$) and Boesten or Boesten/Stroosnijder ($cm^{1/2}$) | 0.63 | 0.58 | 0.71 | 0.63 | 0.58 | 0.71 |
| EGCV | Molar activation energy of degradation ($J\,mol^{-1}$) | 55 000 | 41 250 | 68 750 | 55 000 | 41 250 | 68 750 |
| ENSL | Molar enthalpy of the dissolution process ($J\,mol^{-1}$) | 40 000 | 20 000 | 80 000 | 40 000 | 20 000 | 80 000 |
| G1[a] | Residual moisture content (–) | 0.105 | 0.094 | 0.115 | 0.0012 | 0.0011 | 0.0013 |
| G2[a] | Saturated moisture content (–) | 0.460 | 0.414 | 0.506 | 0.448 | 0.403 | 0.492 |
| G3[a] | Saturated hydraulic conductivity ($cm\,day^{-1}$) | 288 | 72 | 1152 | 98.1 | 24.5 | 392.5 |
| G4[a] | Alpha main drying curve ($cm^{-1}$) | 0.0728 | 0.0692 | 0.0764 | 0.0526 | 0.0500 | 0.0552 |
| G6[a] | Parameter *n* (–) | 1.45 | 1.38 | 1.52 | 1.14 | 1.08 | 1.20 |
| GCTB | Maximum leaf area index (–) | 6.2 | 5.2 | 7.2 | 6.2 | 5.2 | 7.2 |
| HI | Initial pressure heads (cm) | −50 | −71 | −37 | −50 | −141 | −13.5 |
| IF1 | Extinction coefficient for diffuse visible light (–) | 0.6 | 0.3 | 1.2 | 0.6 | 0.3 | 1.2 |

Continued

| Parameter | Description | Wick soil Nominal value | Wick soil Minimum value | Wick soil Maximum value | Hodnet soil Nominal value | Hodnet soil Minimum value | Hodnet soil Maximum value |
|---|---|---|---|---|---|---|---|
| IR1 | Extinction coefficient for direct visible light (–) | 0.750 | 0.375 | 1.5 | 0.750 | 0.375 | 1.5 |
| LEDS | Lengths of dispersion in liquid phase (m) | 0.05 | 0.002 | 0.10 | 0.05 | 0.002 | 0.10 |
| ORG[a] | Organic matter content (–) | 0.029 | 0.025 | 0.032 | 0.020 | 0.017 | 0.022 |
| PSA[a] | Sand content (%) | 0.57 | 0.51 | 0.63 | 0.33 | 0.30 | 0.36 |
| RDD | Root density distribution (–) | 1.0 | 0.75 | 1.0 | 1.0 | 0.75 | 1.0 |
| RDS | Maximum rooting depth allowed by soil profile (cm) | 80 | 60 | 100 | 80 | 60 | 100 |
| RDTB | Maximum rooting depth (cm) | 80 | 60 | 100 | 80 | 60 | 100 |
| RSIG | Minimum rainfall to reset models (cm day$^{-1}$) | 0.50 | 0.25 | 0.75 | 0.50 | 0.25 | 0.75 |
| SUWA | Coefficient of diffusion in water (m$^2$ day$^{-1}$) | $3.97 \times 10^{-5}$ | $8.61 \times 10^{-6}$ | $8.63 \times 10^{-5}$ | $3.97 \times 10^{-5}$ | $8.61 \times 10^{-6}$ | $8.63 \times 10^{-5}$ |
| TEMI | Initial soil temperatures (°C) | 8 | 6 | 10 | 8 | 6 | 10 |
| *Parameterisation specific to Pesticide 1* | | | | | | | |
| NF | Freundlich exponent (–) | 0.90 | 0.72 | 1.08 | 0.90 | 0.72 | 1.08 |
| HL | Half-life (days) | 7.76 | 3.88 | 15.52 | 7.76 | 3.88 | 15.52 |
| KOM | $K_{om}$ (ml g$^{-1}$) | 11.6 | 5.8 | 23.3 | 11.6 | 5.8 | 23.3 |
| *Parameterisation specific to Pesticide 2* | | | | | | | |
| NF | Freundlich exponent (–) | 0.90 | 0.72 | 1.08 | 0.90 | 0.72 | 1.08 |
| HL | Half-life (days) | 23.3 | 11.6 | 46.5 | 23.3 | 11.6 | 46.5 |
| KOM | $K_{om}$ (ml g$^{-1}$) | 58.1 | 29.1 | 116.3 | 58.1 | 29.1 | 116.3 |

[a] Primary parameter to which slave parameters were linked.

## APPENDIX 4
## MACRO input parameters considered in the sensitivity analysis and variation ranges applied

| Parameter | Description | Wick soil Nominal value | Wick soil Minimum value | Wick soil Maximum value | Hodnet soil Nominal value | Hodnet soil Minimum value | Hodnet soil Maximum value |
|---|---|---|---|---|---|---|---|
| *Parameterisation common to Pesticides 1 and 2* | | | | | | | |
| ANNAMP | Temperature annual amplitude (°C) | 8 | 6 | 10 | 8 | 6 | 10 |
| ANNTAV | Average annual temperature (°C) | 8 | 6 | 10 | 8 | 6 | 10 |
| ASCALE[a] | Effective diffusion pathlength (mm) | 20 | 10 | 40 | 20 | 10 | 40 |
| BETA | Root adaptability factor (–) | 0.2 | 0.1 | 0.4 | 0.2 | 0.1 | 0.4 |
| CANCAP | Canopy Interception Capacity (mm) | 2 | 1 | 4 | 2 | 1 | 4 |
| CFORM | Form factor (–) | 1.7 | 1.3 | 2 | 1.7 | 1.3 | 2 |
| CRITAIR | Critical soil air content for root water uptake (%) | 5 | 2 | 8 | 5 | 2 | 8 |
| CTEN[a] | Boundary soil water tension (%) | 10 | 5 | 20 | 18 | 9 | 36 |
| DFORM | Form factor (–) | 0.7 | 0.5 | 0.8 | 0.7 | 0.5 | 0.8 |
| DIFF | Diffusion coefficient in water (m$^2$ s$^{-1}$) | 4.6E-10 | 1E-10 | 1E-09 | 4.6E-10 | 1E-10 | 1E-09 |
| DV | Dispersivity (cm) | 1 | 0.2 | 5 | 1 | 0.2 | 5 |
| EXPB | Exponent moisture relation (–) | 0.70 | 0.42 | 0.98 | 0.70 | 0.42 | 0.98 |
| FEXT | Canopy wash-off coefficient (mm$^{-1}$) | 0.01 | 0.005 | 0.02 | 0.01 | 0.005 | 0.02 |
| FRACMAC | Fraction sorption sites in macropores (–) | 0.02 | 0.005 | 0.1 | 0.02 | 0.005 | 0.1 |
| FREUND | Freundlich exponent (–) | 0.9 | 0.72 | 1.08 | 0.9 | 0.72 | 1.08 |
| GAMMA[a] | Bulk density (g cm$^{-3}$) | 1.35 | 1.21 | 1.48 | 1.39 | 1.25 | 1.52 |
| KSATMIN[a] | Saturated hydraulic conductivity (mm h$^{-1}$) | 120 | 30 | 480 | 39.2 | 19.6 | 78.5 |
| KSM[a] | Boundary hydraulic conductivity (mm h$^{-1}$) | 0.492 | 0.246 | 0.738 | 0.088 | 0.044 | 0.132 |
| LAIHAR | Leaf Area Index at harvest (–) | 1 | 0.5 | 2 | 1 | 0.5 | 2 |
| LAIMAX | Maximum Leaf Area Index (–) | 6.2 | 5.2 | 7.2 | 6.2 | 5.2 | 7.2 |

(*continued overleaf*)

Continued

| Parameter | Description | Wick soil: Nominal value | Wick soil: Minimum value | Wick soil: Maximum value | Hodnet soil: Nominal value | Hodnet soil: Minimum value | Hodnet soil: Maximum value |
|---|---|---|---|---|---|---|---|
| LAIMIN | Leaf Area Index at zdatemin (–) | 1 | 0.5 | 2 | 1 | 0.5 | 2 |
| RINTEN | Rainfall intensity (mm $h^{-1}$) | 2 | 1 | 4 | 2 | 1 | 4 |
| ROOTINIT | Root depth at zdatemin (m) | 0.2 | 0.1 | 0.4 | 0.2 | 0.1 | 0.4 |
| ROOTMAX | Maximum root depth (m) | 0.8 | 0.6 | 1 | 0.8 | 0.6 | 1 |
| RPIN | Root distribution (%) | 70 | 60 | 80 | 70 | 60 | 80 |
| TEMPINI[a] | Initial soil temperature (°C) | 8 | 6 | 10 | 8 | 6 | 10 |
| THETAINI[a] | Initial soil moisture (%) | 27.75 | 20.81 | 34.69 | 27.75 | 20.81 | 34.69 |
| TPORV[a] | Saturated water content (%) | 46.56 | 41.90 | 51.22 | 46.80 | 42.12 | 51.48 |
| TRESP | Exponent temperature response ($K^{-1}$) | 0.08 | 0.06 | 0.1 | 0.08 | 0.06 | 0.1 |
| WATEN | Critical water tension for root water uptake (m) | 5 | 1 | 20 | 5 | 1 | 20 |
| WILT[a] | Wilting point (%) | 10.54 | 9.486 | 11.594 | 16.80 | 15.12 | 18.48 |
| XMPOR[a] | Boundary soil water content (%) | 35.71 | 32.14 | 39.28 | 38.74 | 34.87 | 42.61 |
| ZALP | Correction factor for wet canopy evaporation (–) | 1 | 1 | 1.3 | 1 | 1 | 1.3 |
| ZFINT | Fraction of irrigation intercepted by canopy (–) | 0.1 | 0.05 | 0.2 | 0.1 | 0.05 | 0.2 |
| ZHMIN | Crop height at zdatemin (m) | 0.15 | 0.1 | 0.2 | 0.15 | 0.1 | 0.2 |
| ZLAMB[a] | Pore size distribution index (–) | 0.163 | 0.082 | 0.326 | 0.084 | 0.042 | 0.168 |
| ZM[a] | Tortuosity factor micropores (–) | 0.5 | 0.25 | 1 | 0.5 | 0.25 | 1 |
| ZMIX | Mixing depth (mm) | 1 | 0.25 | 20 | 1 | 0.25 | 20 |
| ZN[a] | Pore size distribution factor for macropores (–) | 4.40 | 3.96 | 4.84 | 4.92 | 3.35 | 6.49 |
| *Parameterisation specific to Pesticide 1* | | | | | | | |
| CANDEG | Canopy degradation rate ($day^{-1}$) | 0.0893 | 0.0446 | 0.1786 | 0.0893 | 0.0446 | 0.1786 |
| DEG[a] | Degradation rates ($day^{-1}$) | 0.0893 | 0.0447 | 0.1786 | 0.0893 | 0.0447 | 0.1786 |
| ZKD[a] | Sorption coefficient ($cm^3\ g^{-1}$) | 0.340 | 0.170 | 0.680 | 0.230 | 0.115 | 0.460 |
| *Parameterisation specific to Pesticide 2* | | | | | | | |
| CANDEG | Canopy degradation rate ($day^{-1}$) | 0.0298 | 0.0149 | 0.0596 | 0.0298 | 0.0149 | 0.0596 |
| DEG[a] | Degradation rates ($day^{-1}$) | 0.0298 | 0.0149 | 0.0596 | 0.0298 | 0.0149 | 0.0596 |
| ZKD[a] | Sorption coefficient ($cm^3\ g^{-1}$) | 1.700 | 0.850 | 3.400 | 1.150 | 0.575 | 2.300 |

[a] Primary parameter to which slave parameters were linked.