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Organic Compounds in the Environment

Sensitivity and First-Step Uncertainty Analyses for the Preferential Flow Model MACRO

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ABSTRACT

Sensitivity analyses for the preferential flow model MACRO were carried out using one-at-a-time and Monte Carlo sampling approaches. Four different scenarios were generated by simulating leaching to depth of two hypothetical pesticides in a sandy loam and a more structured clay loam soil. Sensitivity of the model was assessed using the predictions for accumulated water percolated at a 1-m depth and accumulated pesticide losses in percolation. Results for simulated percolation were similar for the two soils. Predictions of water volumes percolated were found to be only marginally affected by changes in input parameters and the most influential parameter was the water content defining the boundary between micropores and macropores in this dual-porosity model. In contrast, predictions of pesticide losses were found to be dependent on the scenarios considered and to be significantly affected by variations in input parameters. In most scenarios, predictions for pesticide losses by MACRO were most influenced by parameters related to sorption and degradation. Under specific circumstances, pesticide losses can be largely affected by changes in hydrological properties of the soil. Since parameters were varied within ranges that approximated their uncertainty, a first-step assessment of uncertainty for the predictions of pesticide losses was possible. Large uncertainties in the predictions were reported, although these are likely to have been overestimated by considering a large number of input parameters in the exercise. It appears desirable that a probabilistic framework accounting for uncertainty is integrated into the estimation of pesticide exposure for regulatory purposes.

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Much attention has focused on the role of preferential flow in mediating pesticide leaching through soil. There is wide evidence to demonstrate that preferential flow occurs in soils of varying texture (Beven and Germann, 1982; Brown et al., 1995). Preferential flow may result from the presence of macropores (shrinkage cracks and fissures, soil fauna channels, root holes) in structured soils (Beven and Germann, 1982), but also from profile heterogeneities (e.g., horizon boundaries) or water repellency (Hendrickx et al., 1993) in unstructured sandy soils. Relatively rapid movement of water through only a portion of the bulk soil may significantly increase chemical transport by bypassing the soil matrix and decreasing residence time in the upper soil layers where sorption and degradation are generally most important (Brown et al., 2000b). A number of mathematical models have been developed to simulate the transfer of water and solutes in soil resulting from preferential flow phenomena (e.g., Ahuja et al., 1993; Hall, 1993). To date, one of the most widely used is the dual-porosity model MACRO, which divides the soil into micropore and macropore regions (Jarvis, 1994). The model can be set up to simulate a soil where the hydrology is dominated by preferential flow, a soil with no preferential flow at all, or any combination of flow types between these two extremes. MACRO has been used to simulate

Abbreviations: MAROV, maximum absolute ratio of variation; SRRC, standardized rank regression coefficient.

the fate of tracers (e.g., Jabro et al., 1994; Saxena et al., 1994) and pesticides (e.g., Bergström, 1996; Jarvis, 1995; Jarvis et al., 2000) in soils of varying texture.

Pesticide leaching models have a particular application as tools for environmental risk assessment in support of pesticide registration in the European Union. Preferential flow is sometimes considered as a process impacting on leaching to ground water at higher tiers of the assessment scheme where compounds have failed earlier, protective tests. In these instances, MACRO is the main model used in the European Union to assess the impact of preferential flow on pesticide transport. Diffuse losses of pesticides to surface waters in drainflow may result in environmental exposure and MACRO is widely applied to simulate rapid transport of water and chemicals to depth followed by lateral transport by artificial drains (Brown et al., 2000a). MACRO has been coupled to one of the European scenarios to estimate leaching of pesticides to ground water for regulatory purposes (FOCUS, 2000). It will also be the model used to simulate drainflow for aligned scenarios related to the surface water environment (Russell, 2000).

Sensitivity analysis is a key tool to support the use of any model and has applications in model parameterization and in the selection of parameters for calibration and probabilistic modeling. Knowing which model inputs most influence model predictions can also help in the assessment of the quality of a modeling study and in the prioritization of research needs. A first sensitivity analysis for MACRO was carried out by the model developer using a single theoretical scenario (Jarvis, 1991; Jarvis et al., 1991), but it was limited to two lumped scaling factors that could not be measured experimentally. Sensitivity of the model was also investigated from simulations of the leaching of dichlorprop to 1 m in lysimeters (Jarvis, 1991), but the extreme character of the soil (heavy clay, clay content 46–61%) raises some doubts over the applicability of the results to less structured soils. The information on the sensitivity of the model is therefore rather limited despite the model being widely used both by the research community and within pesticide registration schemes. In this paper, we present the results of a sensitivity analysis for the MACRO model using four contrasting scenarios and two different investigation methods: a first-step one-at-a-time sensitivity analysis and a technique based on Monte Carlo sampling.

METHODS

Description of the Model

MACRO (Version 4.1) is a physically based preferential flow model with the total soil porosity divided into two flow domains (macropores and micropores), each characterized by a flow rate and solute concentration (Jarvis, 1994). Soil water flow and solute transport in the micropores is modeled 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. In situations where preferential flow is unlikely to occur, the model reverts to the classical solution of Richards' equation and the convection–dispersion equation. At the surface boundary, the infiltrating water is partitioned between micropores and macropores depending on the infiltration capacity of the micropores and the net rainfall intensity. Exchange between micropores and macropores is calculated according to approximate, physically based expressions using an effective aggregate half-width. A range of bottom boundary conditions is available to the user. Soil temperatures are calculated from air temperatures using the heat conduction equation.

Crop development is based on a simple model that uses dates for emergence, maximum leaf area, and harvest. Root depth and crop height are assumed to increase linearly up to the stage where the crop has a maximum leaf area and are then considered constant until harvest. For perennials, the two variables are assumed constant during the simulation. Root water uptake is calculated as a function of the evaporative demand, soil water content, and root distribution. Although water uptake can occur in both regions, the water is preferentially extracted from the macropores.

Pesticide degradation is modeled using first-order kinetics. Degradation half-lives need to be specified for the solid and liquid phase of the macropores and micropores, and may be adjusted for temperature and moisture effects. Sorption is assumed to be at instantaneous equilibrium and to be described by a Freundlich isotherm. The magnitude of sorption is assumed to be similar in both pore domains, but the user must specify the distribution of sorption sites between the two. Time-dependent sorption can be simulated by changing the sorption characteristics at a number of dates during the simulation.

The model can be used to describe water and solute transport in a variety of soil types, but the processes of finger flow and funnel flow in coarse-textured soils cannot be simulated. MACRO has been tested against several field and lysimeter studies with a number of different pesticides including dichlorprop and bentazone in Sweden (Jarvis et al., 1994); dichlorprop, MCPA, and 2,4-D in Denmark (Miljøstyrelsen, 1994); simazine, methabenzthiazuron, and metamitron in Germany (Jarvis, 1995); and chlorsulfuron in Sweden (Bergström, 1996). These evaluations were based on the calibration of a number of parameters and, under these conditions, the model was generally shown to give a reasonable match to observed behavior. A broad conclusion is that MACRO, in common with other preferential flow models, requires careful calibration before it can be used with confidence as a management tool (Bergström and Jarvis, 1994). Despite the widespread interest in using MACRO, the model remains difficult to parameterize (Brown et al., 2000a). Lack of knowledge and adequate measurement techniques, approximations, inaccuracies, and inherent variability result in uncertainty in the selection of values for a significant number of parameters, in common with other environmental fate models.

Parameterization of the Base-Case Scenarios

In sensitivity and uncertainty analyses, base-case scenarios are defined as the initial sets of model input and output from which the variations of parameters are applied. Results from sensitivity analyses have been shown to be dependent on the base-case scenarios considered (Ferreira et al., 1995). In order to represent a significant range of variation in environmental conditions, four scenarios were compiled by simulating the fate of two hypothetical pesticides in two soils of contrasting properties. The influence of small variations in conditions are addressed by the sensitivity analyses themselves, which consider variations around the initial values.

Weather data were selected from 30-year records for Silsoe

Table 1. Selected properties of the Wick and Hodnet soils.

Depth	Organic carbon	Sand	Silt	Clay	Texture†	Bulk density	pH (H_2O)
cm	%					g cm^{-3}	
			Wick soil				
0–20	1.70	57	33	10	SL	1.35	6.5
20–50	0.80	70	20	10	SL	1.45	7.0
50–75	0.30	73	16	11	SL	1.41	7.0
75–100	0.20	77	9	14	SL	1.53	6.9
			Hodnet soil				
0–33	1.15	33	48	19	CL	1.39	6.7
33–60	0.48	42	42	16	ZCL	1.62	6.8
60–80	0.40	29	48	23	CL	1.55	6.8
80–100	0.30	26	55	19	CL	1.48	6.8

† Texture is given according to the UK classification: SL, sandy loam; CL, clay loam; ZCL, silty clay loam.

Table 2. Water retention data for the Wick and Hodnet soils.

Depth	Volumetric water content at a tension of					
	0 kPa	5 kPa	10 kPa	40 kPa	200 kPa	1500 kPa
cm	%					
			Wick soil			
0–20	46.6	27.8	24.1	19.7	15.1	10.5
20–50	39.6	19.1	17.0	14.2	10.8	7.9
50–75	39.0	14.7	11.7	8.7	6.0	4.4
75–100	34.3	19.2	16.4	13.4	9.8	7.7
			Hodnet soil			
0–33	46.8	34.9	33.7	31.2	25.1	16.8
33–60	38.8	30.8	29.9	26.7	24.2	17.9
60–80	41.5	32.2	31.4	28.9	24.5	19.9
80–100	44.0	35.8	35.0	31.8	26.6	20.1

(Bedfordshire, UK). Annual average rainfall over the period 1965 to 1994 ranged from 413 to 854 mm (mean 573 mm; median 572 mm). The year 1979 was chosen as being a wet year for this location (annual rainfall 700 mm), especially during the spring and winter periods. Potential evapotranspiration was calculated outside the model using the Penman–Monteith equation (FAO, 1991). The data for 1979 were repeated as many times as required to allow the full pesticide leaching breakthrough to occur. The repetition of the same climate information meant that the comparison between modeling scenarios with different running times was still meaningful.

Soils that were considered in the base-case scenarios were of the Wick and Hodnet series. Soils from the Wick series are deep, uniformly coarse-textured, free draining sandy loams formed on loose, sandy, or sandy gravelly glacial, fluvoglacial, or river terrace deposits. 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 Hodnet series are deep, fine loamy soils formed on interbedded reddish sandstones and mudstones. They have slowly permeable horizons in the subsoil, which restrict the downward percolation of water and these soils are occasionally waterlogged. Structural macropores in the Hodnet soil often provide pathways for rapid, preferential transport of water and associated solutes to depth (Beulke et al., 1999). Selected properties of the two soils are presented in Tables 1 and 2. Water retention data were measured using the standard methods for England and Wales (Avery and Bascomb, 1982). Profile depths for the two soils were set to 1 m to allow comparison of results between the two soils and to tie in with current regulatory practice in the European Union, where concentrations in water percolating at a 1-m depth are used as a protective indicator for concentrations in ground water.

Where possible, selection of values for input parameters was based on measured data for these two series. Some hydraulic parameters were selected by expert judgement on the basis of values used for similar soils where calibration data were available. The uncertainty was relatively large for base-case parameters selected by expert judgement and this was later reflected in the range of variation used within the sensitivity analysis. Parameters were chosen as follows. The pore size distribution index in the micropores (ZLAMB) was calculated by fitting the Brooks and Corey equation (Brooks and Corey, 1964) to the measured water release curve. Expert judgement was used to establish the water tension at the boundary between micropores and macropores (CTEN), as this cannot readily be independently estimated. The water content equivalent to this tension (XMPOR) was then derived from the measured water release curve, while the conductivity at the boundary (KSM) was estimated from the above values using the equation given by Laliberte et al. (1968) and Jarvis et al. (1997). The pore size distribution index in the macropores (ZN) was calculated from CTEN using equations built into MACRO_DB (Jarvis et al., 1997). The saturated hydraulic conductivity was derived using the pedotransfer functions for soils in England and Wales by Hollis and Woods (1989). Aggregate half-widths were selected from basic descriptions of soil structure using the rules proposed by Jarvis et al. (1997). The bottom boundary condition was set to a constant hydraulic gradient of 1 for the two soils. The clay loam was considered to be effectively free draining because of the presence of preferential flow pathways.

Pesticide properties were selected to ensure that some leaching to a 1-m depth was predicted. Pesticide 1 has a K_{oc} of 20 mL g^{-1} and a laboratory half-life in soil of 7.8 d at 20°C (equivalent to a half-life of 20 d at 8°C). Pesticide 2 has a K_{oc} of 100 mL g^{-1} and a laboratory half-life in soil of 23.3 d at 20°C (equivalent to a half-life of 60 d at 8°C). Sorption of the two pesticides was assumed to be characterized by a Freundlich exponent of 0.9 and was considered to be proportional to the organic carbon content in the different horizons. Although values of K_{oc} and half-lives for the two pesticides were chosen on a subjective basis, a comparison with pesticide properties for compounds registered in the UK (Lewis and Bardon, 1998) showed that these properties were realistic (Fig. 1). The pa-

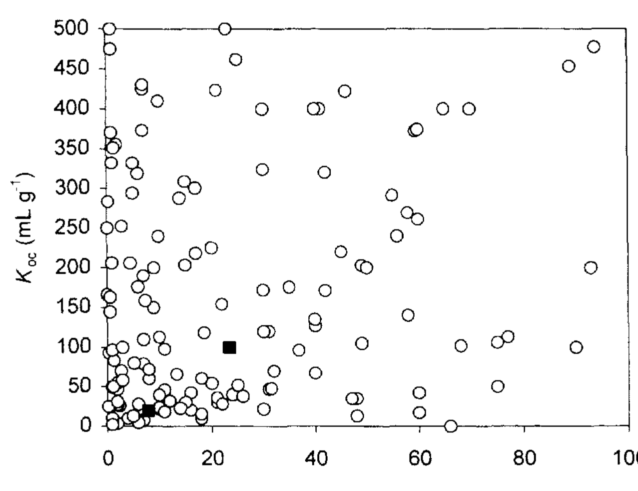

Fig. 1. Comparison between K_{oc} and DT50 values of the two theoretical pesticides considered in the present study (closed squares) and those for pesticides registered for use in the UK (open circles). Properties for registered compounds were taken from Lewis and Bardon (1998). Only those registered pesticides with K_{oc} < 500 mL g^{-1} and DT50 < 100 d are shown.

rameter describing the relative proportion of sorption sites in the micropore and macropore regions (FRACMAC) was set to 0.02 (i.e., 2% of sorption sites are in the macropore domain). A simplified degradation scheme assuming transformation of the parent products without formation of major metabolites was considered. Degradation rates in the subsoil were corrected from that for the topsoil using the equation presented by Jarvis et al. (1997). The two products were considered to be applied to soil (i.e., no crop interception was considered) at an application rate of 2 kg a.i. ha^{-1} on 1 November of the first year of simulation. The simulated crop was winter wheat (*Triticum aestivum* L.) in each year and this was considered to emerge on 12 October and to be harvested on 7 August the next year. Crop maturation was considered to occur on 24 June. Values for crop parameters were derived from calibrated values available in the MACRO_DB system (Jarvis et al., 1997).

Preliminary investigations showed that the minimum time to allow complete disappearance of the two compounds from the water moving to a 1-m depth for three scenarios was four years. For the scenario describing the leaching of Pesticide 2 in the Wick soil, this was not sufficient and six-year runs were considered. Model outputs used for assessment of the sensitivity of the model were accumulated water percolation (in mm) and pesticide leaching (in g ha^{-1}) at a 1-m depth for the sandy loam and clay loam soil.

Assessment of Sensitivity

Both one-at-a-time and Monte Carlo sensitivity analyses were carried out. One-at-a-time sensitivity analysis consists of varying selected parameters one after the other (all other parameters being kept constant at their nominal value) and observing the influence of the changes on model predictions (Hamby, 1994). In contrast, Monte Carlo sensitivity analysis involves the modification of values for all selected input parameters at the same time using Monte Carlo sampling from predefined probability density functions.

There are a number of reasons why Monte Carlo approaches are often used for investigating the sensitivity of environmental models. First, they allow for the simultaneous variation of the values of all the input parameters (Blower and Dowlatabadi, 1994), in contrast to the conceptually simpler one-at-a-time sensitivity analysis. Second, they are relatively simple to conduct when using appropriate software (Hamby, 1995). Third, the use of an efficient sampling scheme (such as the Latin hypercube sampling; McKay et al., 1979) greatly decreases the number of runs required. Fourth, Monte Carlo approaches may avoid the attribution of specific values to each parameter in a model as in the one-at-a-time sensitivity analysis. If parameters are varied within their uncertainty range, the Monte Carlo approach to sensitivity analysis can provide a simultaneous assessment of uncertainty.

In contrast to some other sensitivity studies that concentrated a priori on the most sensitive parameters (e.g., Boesten and van der Linden, 1991), the number of input parameters considered for variation here was maximized. Where little information is available on the sensitivity of the model, good confidence in the sensitivity results may be jeopardized if the parameters to be included are chosen a priori. Variation of input parameters (for the one-at-a-time approach) and probability density functions (for the approach based on Monte Carlo sampling) were attributed by expert judgement by three individuals with significant experience in pesticide fate modeling with the MACRO model (S. Beulke, C.D. Brown, I.G. Dubus). Each parameter was assigned a range of uncertainty reflecting the source of information for its derivation, the range of uncertainty associated with the attribution of values by expert judgement, and likely spatial field variability and measurement error where appropriate. Parameters were not allowed to vary outside these ranges. The approach that was followed therefore differed from that where parameters are varied by a standard variation irrespective of their uncertainty (Hamby, 1994). Tables 3 and 4 present the list of parameters that were varied, together with their variation range and the probability density functions for the four scenarios. For the one-at-a-time sensitivity analysis, variation increments were broadly proportional to the variation applied (typically two 5% increments, 25% increments from 25 to 100% variations, then 100% increments for any larger variations). For the Monte Carlo approach, normal distributions were assigned to parameters for which a symmetrical variation was expected. The more uncertain parameters and those which show a large variability in the laboratory or in the field were considered to be log-normally distributed. Uniform distributions were attributed to parameters for which variation was considered to differ from the normal and log-normal distributions. Investigations related to the influence of the attribution of probability distribution functions on sensitivity results were considered to be outside the scope of the present study. A number of "slave" input parameters were linked to the 43 primary input parameters (for instance, K_d values in the subsoil horizons were related to those in the topsoil) and this resulted in a variation of a total of 99 input parameters in the model. When a primary parameter to which slaves were linked was varied, relevant slave parameters were modified by the same extent. The change of input parameters, the running of the model, and the extraction of model results were automated using the SENSAN program (Doherty et al., 1994).

Sensitivity of the model to changes in input parameters was assessed numerically for the one-at-a-time sensitivity analysis by the maximum ratio of variation of the model output and the variation of the model input. For comparison purposes, the absolute value of these ratios was taken and the maximum absolute ratio of variation (MAROV) index for each parameter was derived as:

$$\mathrm{MAROV} = \mathrm{Max}\left|\frac{(O - O_{\mathrm{BC}})}{(I - I_{\mathrm{BC}})} \times \frac{(I_{\mathrm{BC}})}{(O_{\mathrm{BC}})}\right| \quad [1]$$

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

The larger the MAROV for a parameter, the larger the potential influence of that parameter on model output. A MAROV of unity means that a variation in the model input by x% will result at most in the same variation (x%) in the model output.

For the Monte Carlo sensitivity analysis, 250 input files were generated for each scenario using Latin hypercube sampling (LHS; McKay et al., 1979) from probability density functions (UNCSAM; Janssen et al., 1994). Different seed numbers were supplied to the sampling package for each scenario. The LHS technique was used, as it provides an efficient sampling scheme that enables the number of runs to be kept to a minimum (Blower and Dowlatabadi, 1994). In order to avoid the use of unrealistic values for input parameters, sampling was only allowed to occur in the range defined by the minimum and maximum values used in the one-at-a-time sensitivity analysis. No correlations were specified between primary input parameters because of the lack of specific data on the relationship between variables. For each scenario, input parameters and results of the 250 runs were standardized (i.e., the population mean was subtracted from the individual results and the re-

Table 3. Model parameterization for Pesticides 1 and 2 on the Wick scenario and variation of parameters for the one-at-a-time and Monte Carlo approaches.

Parameter	Description	One-at-a-time			Monte Carlo	
		Nominal value	Minimum value	Maximum value	Distribution	Variance
		Parameterization common to Pesticides 1 and 2				
ANNAMP	temperature annual amplitude, °C	8	6	10	normal	1.04
ANNTAV	average annual temperature, °C	8	6	10	normal	1.04
ASCALE†	effective diffusion pathlength, mm	20	10	40	log-normal	4.50×10^{1}
BETA	root adaptability factor, unitless	0.2	0.1	0.4	log-normal	4.50×10^{-3}
CANCAP	canopy interception capacity, mm	2	1	4	log-normal	4.50×10^{-1}
CFORM	form factor, unitless	1.7	1.3	2	normal	2.34×10^{-2}
CRITAIR	critical soil air content for root water uptake, %	5	2	8	normal	2.34
CTEN†	boundary soil water tension, %	10	5	20	log-normal	1.12×10^{1}
DFORM	form factor, unitless	0.7	0.5	0.8	normal	2.60×10^{-3}
DIFF	diffusion coefficient in water, $m^2\ s^{-1}$	4.6×10^{-10}	1×10^{-10}	1×10^{-9}	normal	3.53×10^{-20}
DV	dispersivity, cm	1	0.2	5	log-normal	6.26×10^{-1}
EXPB	exponent moisture relation, unitless	0.70	0.42	0.98	normal	2.04×10^{-2}
FEXT	canopy wash-off coefficient, mm^{-1}	0.01	0.005	0.02	log-normal	1.12×10^{-5}
FRACMAC	fraction sorption sites in macropores, unitless	0.02	0.005	0.1	log-normal	1.82×10^{-4}
FREUND	Freundlich exponent, unitless	0.9	0.72	1.08	normal	8.43×10^{-3}
GAMMA†	bulk density, $g\ cm^{-3}$	1.35	1.21	1.48	normal	4.74×10^{-3}
KSATMIN†	saturated hydraulic conductivity, $mm\ h^{-1}$	120	30	480	log-normal	1.62×10^{3}
KSM†	boundary hydraulic conductivity, $mm\ h^{-1}$	0.492	0.246	0.738	normal	1.58×10^{-2}
LAIHAR	leaf area index at harvest, unitless	1	0.5	2	log-normal	1.12×10^{-1}
LAIMAX	maximum leaf area index, unitless	6.2	5.2	7.2	normal	2.60×10^{-1}
LAIMIN	leaf area index at zdatemin, unitless	1	0.5	2	normal	6.51×10^{-2}
RINTEN	rainfall intensity, $mm\ h^{-1}$	2	1	4	log-normal	4.50×10^{-1}
ROOTINIT	root depth at zdatemin, m	0.2	0.1	0.4	normal	2.60×10^{-3}
ROOTMAX	maximum root depth, m	0.8	0.6	1	normal	1.04×10^{-2}
RPIN	root distribution, %	70	60	80	normal	2.60×10^{-1}
TEMPINI†	initial soil temperature, °C	8	6	10	normal	1.04
THETAINI†	initial soil moisture, %	27.75	20.81	34.69	normal	1.25×10^{1}
TPORV†	saturated water content, %	46.56	41.90	51.22	normal	5.64
TRESP	exponent temperature response, $°K^{-1}$	0.08	0.06	0.1	normal	1.04×10^{-4}
WATEN	critical water tension for root water uptake, m	5	1	20	uniform	–
WILT†	wilting point, %	10.54	9.486	11.594	normal	2.89×10^{-1}
XMPOR†	boundary soil water content, %	35.71	32.14	39.28	normal	3.32
ZALP	correction factor for wet canopy evaporation, unitless	1	1	1.3	uniform	–
ZFINT	fraction of irrigation intercepted by canopy, unitless	0.1	0.05	0.2	log-normal	1.12×10^{-3}
ZHMIN	crop height at zdatemin, m	0.15	0.1	0.2	normal	6.51×10^{-4}
ZLAMB†	pore size distribution index, unitless	0.163	0.082	0.326	log-normal	2.99×10^{-3}
ZM†	tortuosity factor micropores, unitless	0.5	0.25	1	log-normal	2.81×10^{-2}
ZMIX	mixing depth, mm	1	0.25	20	log-normal	4.54×10^{-1}
ZN†	pore size distribution factor for macropores, unitless	4.40	3.96	4.84	normal	5.16×10^{-1}
		Parameterization specific to Pesticide 1				
CANDEG	canopy degradation rate, d^{-1}	0.0893	0.0446	0.1786	log-normal	8.97×10^{-4}
DEG†	degradation rates, d^{-1}	0.0893	0.0447	0.1786	log-normal	8.97×10^{-4}
ZKD†	sorption coefficient, $cm^3\ g^{-1}$	0.34	0.17	0.68	log-normal	1.30×10^{-2}
		Parameterization specific to Pesticide 2				
CANDEG	canopy degradation rate, d^{-1}	0.0298	0.0149	0.0596	log-normal	9.99×10^{-5}
DEG†	degradation rates, d^{-1}	0.0298	0.0149	0.0596	log-normal	9.99×10^{-5}
ZKD†	sorption coefficient, $cm^3\ g^{-1}$	1.7	0.85	3.4	log-normal	3.25×10^{-1}

† Primary parameter to which slave parameters were linked.

sulting difference was divided by the standard deviation of the population) and then ranked. The standardization was aimed at removing the influence of differences in units and in the relative magnitude of parameters. The rank transformation was intended to reduce the effects of nonlinearity on the assessment of sensitivity (Iman and Conover, 1979). Standardized and ranked model predictions for pesticide losses were related to standardized and ranked model inputs using multiple linear regressions:

$$Y = \sum_{i=1}^{k} b_i \times X_i + \varepsilon \qquad [2]$$

where Y is a standardized model output, X_i is a standardized input parameter, b_i is the regression coefficient for each X_i, ε is the regression error, and k is the number of input parameters varied in the sensitivity analysis.

The magnitude of the regression coefficients of the regression (or standardized rank regression coefficients, SRRC) allows a comparison of the relative contribution of each input parameter in the prediction of the model (Hamby, 1994). Sensitivity of the model to each input parameter was thus assessed using SRRC values for this particular input parameter. The larger the SRRC for a parameter, the more influence on model predictions this parameter has.

RESULTS AND DISCUSSION

Base-Case Scenarios

The four base-case scenarios resulted from the modeling of the fate of the two compounds in the two soil types. Annual and cumulative water percolation and pesticide losses for each scenario are presented in Table 5. Percolation for the two soils was very similar, with a difference of 12 to 13 mm in the annual predicted volumes of water. Smaller percolation volumes were pre-

Table 4. Model parameterization for Pesticides 1 and 2 on the Hodnet scenario and variation of parameters for the one-at-a time and Monte Carlo approaches.

Parameter	Description	One-at-a-time			Monte Carlo	
		Nominal value	Minimum value	Maximum value	Distribution	Variance
		Parameterization common to Pesticides 1 and 2				
ANNAMP	temperature annual amplitude, °C	8	6	10	normal	1.04
ANNTAV	average annual temperature, °C	8	6	10	normal	1.04
ASCALE†	effective diffusion pathlength, mm	20	10	40	log-normal	4.50×10^{1}
BETA	root adaptability factor, unitless	0.2	0.1	0.4	log-normal	4.50×10^{-3}
CANCAP	canopy interception capacity, mm	2	1	4	log-normal	4.50×10^{-1}
CFORM	form factor, unitless	1.7	1.3	2	normal	2.34×10^{-2}
CRITAIR	critical soil air content for root water uptake, %	5	2	8	normal	2.34
CTEN†	boundary soil water tension, %	18	9	36	log-normal	3.64×10^{1}
DFORM	form factor, unitless	0.7	0.5	0.8	normal	2.60×10^{-3}
DIFF	diffusion coefficient in water, $m^2\ s^{-1}$	4.6×10^{-10}	1×10^{-10}	1×10^{-9}	normal	3.53×10^{-20}
DV	dispersivity cm	1	0.2	5	log-normal	6.26×10^{-1}
EXPB	exponent moisture relation, unitless	0.70	0.42	0.98	normal	2.04×10^{-2}
FEXT	canopy wash-off coefficient, mm^{-1}	0.01	0.005	0.02	log-normal	1.12×10^{-5}
FRACMAC	fraction sorption sites in macropores, unitless	0.02	0.005	0.1	log-normal	1.82×10^{-4}
FREUND	Freundlich exponent, unitless	0.9	0.72	1.08	normal	8.43×10^{-3}
GAMMA†	bulk density, $g\ cm^{-3}$	1.39	1.25	1.52	normal	5.03×10^{-3}
KSATMIN†	saturated hydraulic conductivity, $mm\ h^{-1}$	39.2	19.6	78.5	log-normal	1.73×10^{2}
KSM†	boundary hydraulic conductivity, $mm\ h^{-1}$	0.088	0.044	0.132	normal	5.04×10^{-4}
LAIHAR	leaf area index at harvest, unitless	1	0.5	2	log-normal	1.12×10^{-1}
LAIMAX	maximum leaf area index, unitless	6.2	5.2	7.2	normal	2.60×10^{-1}
LAIMIN	leaf area index at zdatemin, unitless	1	0.5	2	normal	6.51×10^{-2}
RINTEN	rainfall intensity, $mm\ h^{-1}$	2	1	4	log-normal	4.50×10^{-1}
ROOTINIT	root depth at zdatemin, m	0.2	0.1	0.4	normal	2.60×10^{-3}
ROOTMAX	maximum root depth, m	0.8	0.6	1	normal	1.04×10^{-2}
RPIN	root distribution, %	70	60	80	normal	2.60×10^{1}
TEMPINI†	initial soil temperature, °C	8	6	10	normal	1.04
THETAINI†	initial soil moisture, %	27.75	20.81	34.69	normal	1.25×10^{1}
TPORV†	saturated water content, %	46.80	42.12	51.48	normal	5.70
TRESP	exponent temperature response, $°K^{-1}$	0.08	0.06	0.1	normal	1.04×10^{-4}
WATEN	critical water tension for root water uptake, m	5	1	20	uniform	–
WILT†	wilting point, %	16.80	15.12	18.48	normal	7.35×10^{-1}
XMPOR†	boundary soil water content, %	38.74	34.87	42.61	normal	3.91
ZALP	correction factor for wet canopy evaporation, unitless	1	1	1.3	uniform	–
ZFINT	fraction of irrigation intercepted by canopy, unitless	0.1	0.05	0.2	log-normal	1.12×10^{-3}
ZHMIN	crop height at zdatemin, m	0.15	0.1	0.2	normal	6.51×10^{-4}
ZLAMB†	pore size distribution index, unitless	0.084	0.042	0.168	log-normal	7.94×10^{-4}
ZM†	tortuosity factor micropores, unitless	0.5	0.25	1	log-normal	2.81×10^{-2}
ZMIX	mixing depth, mm	1	0.25	20	log-normal	4.54×10^{-1}
ZN†	pore size distribution factor for macropores, unitless	4.92	3.35	6.49	normal	6.45×10^{-1}
		Parameterization specific to Pesticide 1				
CANDEG	canopy degradation rate, d^{-1}	0.0893	0.0446	0.1786	log-normal	8.97×10^{-4}
DEG†	degradation rates, d^{-1}	0.0893	0.0447	0.1786	log-normal	8.97×10^{-4}
ZKD†	sorption coefficient, $cm^3\ g^{-1}$	0.230	0.115	0.460	log-normal	5.95×10^{-3}
		Parameterization specific to Pesticide 2				
CANDEG	canopy degradation rate, d^{-1}	0.0298	0.0149	0.0596	log-normal	9.99×10^{-5}
DEG†	degradation rates, d^{-1}	0.0298	0.0149	0.0596	log-normal	9.99×10^{-5}
ZKD†	sorption coefficient, $cm^3\ g^{-1}$	1.150	0.575	2.300	log-normal	1.49×10^{-1}

† Primary parameter to which slave parameters were linked.

dicted in the first year because of the delay in the model reaching equilibrium. A model pre-run of one year prior to the assessment of the sensitivity was not possible because of the expected 20% increase (namely, 10.5 d) in the total running time. The slightly larger percolation of water in the fourth year of simulation can be attributed to the presence of a leap year. Total pesticide losses were predicted to range from about 34 to 40 g ha^{-1} for Pesticide 1 and from 7.5 to about 87 g ha^{-1} for Pesticide 2. These quantities correspond to a loss of 0.4 to 4.4%

Table 5. Annual and accumulated water percolation and pesticide losses for the four base-case scenarios.

Year	Water percolation				Pesticide losses			
	Wick		Hodnet		Wick		Hodnet	
	Pesticide 1	Pesticide 2	Pesticide 1	Pesticide 2	Pesticide 1	Pesticide 2	Pesticide 1	Pesticide 2
	mm				g ha^{-1}			
1	242	242	230	230	0.02	<0.01	23.87	51.06
2	283	283	271	271	29.80	1.45	15.83	33.61
3	283	283	271	271	3.99	4.10	0.11	2.47
4	286	286	273	273	0.01	1.60	<0.01	0.15
5	–	283	–	–	–	0.32	–	–
6	–	283	–	–	–	0.05	–	–
Total	1094	1660	1045	1045	33.8	7.5	39.8	87.3

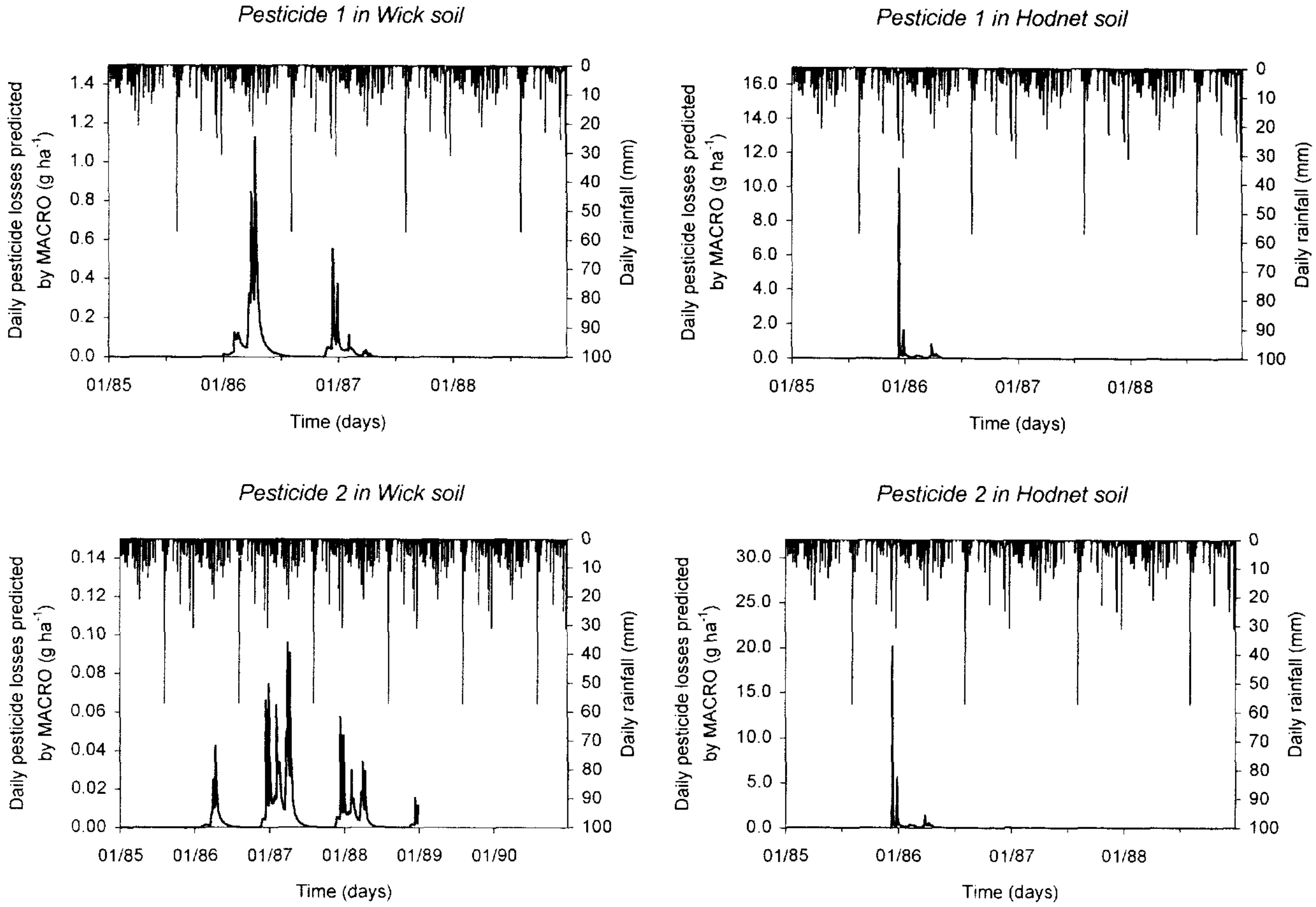

Fig. 2. Rainfall data and pesticide leaching breakthrough at a 1-m depth predicted by MACRO for the four base-case scenarios.

of the 2 kg ha^{-1} of active substance applied. Maximum daily pesticide losses were predicted 43 days after treatment (DAT) for the Hodnet scenarios, 163 DAT for the Pesticide 1 on Wick scenario, and 516 DAT for the scenario involving Pesticide 2 and the Wick soil. Predicted losses for the two individual pesticides were larger in the clay loam than in the sandy loam, especially for Pesticide 2 (87 g ha^{-1} compared with 7.5 g ha^{-1}, respectively). Larger losses from the clay loam were also observed in lysimeter experiments carried out using these two soils (Beulke et al., 1999). The Hodnet soil has a larger clay content and more highly developed structure than the Wick soil and is thus more prone to preferential flow between structural voids. Preferential flow can be expected to make a significant contribution to total leaching of pesticides and sharp differentiation in extent of leaching can be observed for contrasting soils, particularly for more strongly sorbed compounds (Larsson and Jarvis, 2000). Losses for Pesticide 1 were predicted to be larger than those for Pesticide 2 in the Wick soil, which suggests that the strength of sorption may be a primary factor determining pesticide leaching in this soil. In contrast, the larger losses for Pesticide 2 in the Hodnet soil suggest that the persistence (i.e., time of availability for leaching) may be more important than sorption in this clay loam.

Figure 2 presents daily pesticide losses predicted by the MACRO model for each of the four base-case scenarios. A clear distinction in the breakthrough curves between the two soils can be made. In the Wick soil, losses by leaching extended over a few years and were predicted to last for five to eight months each year. Total loss by leaching was predicted to take place over two years for Pesticide 1 and four years for Pesticide 2. 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 (up to 20 g a.i. ha^{-1}). Transient losses of chemical are typical of situations where preferential flow plays an important role in transfer through the soil profile (Brown et al., 1995). Major leaching events in the Wick soil were associated with rainfall in April and December while the only significant leaching for the Hodnet soil resulted from a series of rainfall events (58 mm in a week) in mid-December in the second year of simulation.

Results for the One-at-a-Time Sensitivity Analysis

MACRO Predictions for Water Percolation

A total of 1436 runs was carried out to assess the sensitivity of the MACRO model to changes in input parameters using the one-at-a-time variation approach. Twenty-three out of the 46 parameters that were varied had an influence on the MACRO predictions for vol-

Table 6. Classification of MACRO input parameters according to their influence on the prediction of accumulated water percolated to a 1-m depth (one-at-a-time approach). Parameters are classified by decreasing influence according to their maximum absolute ratio of variation (MAROV) value. A brief description of the parameters is provided in Table 3.

	Wick soil		Hodnet soil	
	Parameter	MAROV	Parameter	MAROV
1	XMPOR	0.728	XMPOR	0.856
2	RPIN	0.274	RPIN	0.371
3	ROOTMAX	0.226	THETAINI	0.320
4	THETAINI	0.181	WILT	0.300
5	WILT	0.153	ROOTMAX	0.280
6	ZALP	0.122	TPORV	0.236
7	ZLAMB	0.114	ZALP	0.133
8	CTEN	0.113	CTEN	0.095
9	KSM	0.042	ZLAMB	0.054
10	TPORV	0.034	BETA	0.054
11	BETA	0.033	ZN	0.049
12	ZN	0.014	GAMMA	0.021
13	WATEN	0.013	LAIMAX	0.018
14	GAMMA	0.012	KSATMIN	0.015
15	LAIMAX	0.011	RINTEN	0.007

umes of water percolated at a 1-m depth. Table 6 presents the 15 most influential parameters for the Wick and Hodnet soils. The maximum value for the sensitivity index for percolation (0.86 for the parameter XMPOR; Hodnet soil) was below unity, which means that a variation in the input parameters will be attenuated through the model (e.g., a variation of the input by 10% would result in variation in predicted percolation of less than 10%). Little difference in the classification of parameters and the magnitude of sensitivity was noted between the soil scenarios with the 15 most influential parameters very similar. The parameter that most influenced prediction of percolation was XMPOR, a parameter specific to the dual-porosity MACRO model, which represents the water content at the boundary between the micropore and macropore flow domains. This parameter is the water content corresponding to a tension of CTEN and is determined either graphically or using a mathematical description of the water release curve (e.g., the Brooks and Corey equation). The CTEN parameter can either be set by determining the inflection point in the curve relating the hydraulic conductivity to the soil water tension or, where data do not allow this, by expert judgement in relation to soil texture. The parameters CTEN, XMPOR, and the hydraulic conductivity at the micropore–macropore boundary (parameter KSM) partly determine the extent of preferential flow in MACRO. Although the three parameters are numerically related, they were varied independently here to allow a full one-at-a-time evaluation of sensitivity. Parameters related to the description of the geometry of the rooting system (RPIN, the percentage of root length in the top 25% of the root depth and ROOTMAX, the maximum rooting depth) were found to influence predictions of percolation to a lesser extent. The presence in the few most influential parameters of the volumetric water content at the start of the simulation (THETAINI) is somewhat artificial since no pre-run period to allow the model to equilibrate was included in the modeling.

Although meteorological inputs were not included in the sensitivity analysis (i.e., data on potential evapotranspiration were treated as certain inputs), it is expected that the balance between rainfall and evapotranspiration will be the main determinant for percolation volumes. Rainfall data are often considered as a certain variable, but they are subject to uncertainties (Krajewski et al., 1998). Goodrich et al. (1995) assessed the uncertainty in rainfall data due to sampling equipment and demonstrated that the assumption usually made of spatial rainfall uniformity at the small watershed scale did not hold for a 4.4-ha catchment characterized by convective thunderstorms. It is common practice to estimate daily potential evapotranspiration (PET) outside leaching models using different equations, but the choice of a particular equation is likely to influence PET estimations. Jensen et al. (1990) analyzed and compared the performance of 20 different methods using evaporation data for 11 locations and found relative differences of −18% to +35%. The multiplicity of existing equations results in a large uncertainty being associated with potential evapotranspiration data and this will transfer into uncertainty in predictions for percolation volumes.

MACRO Predictions for Pesticide Losses

Thirty-nine out of the 43 parameters considered in this study were found to influence predictions of cumulative pesticide losses by MACRO. Pesticide losses were affected by a larger number of parameters compared with percolation (37 vs. 24 parameters). The magnitude of the sensitivity of percolation and pesticide losses differed significantly. Maximum values for the sensitivity index for pesticide losses ranged from 3.1 to 22.2 (Table 7) and the sensitivity ranking of input parameters according to their influence on pesticide loads was found to vary between the different scenarios. The value of 22.2 was derived for the Freundlich exponent for which a variation of 20% (from 0.9 to 1.08) resulted in an increase of pesticide losses from 7.5 to 40.9 g ha^{-1}. Figure 3 provides a graphical representation of the results in which parameters have been classified into broad groupings (sorption, degradation, hydrology–soil, cropping, and miscellaneous parameters).

Total losses of the two pesticides in the sandy loam were mostly affected by parameters related to pesticide sorption (Freundlich distribution coefficient ZKD and Freundlich exponent FREUND) and degradation (degradation rates in the different compartments DEG and to a lesser extent, the exponent in the temperature response curve for degradation TRESP). The large influence of these parameters on predictions of pesticide leaching models has been previously reported elsewhere (Boesten and van der Linden, 1991). These processes are believed to contribute to a large extent to the uncertainty of model predictions as they show a large variability (a variation by a factor of two is not uncommon for degradation rates or Freundlich distribution coefficients).

For the two scenarios involving the more structured clay loam soil, parameters related to the description of the soil hydrology were found to have a larger relative

Table 7. Classification of MACRO input parameters according to their influence on the prediction of pesticide losses at a 1-m depth (one-at-a-time approach). Parameters are classified by decreasing influence according to their maximum absolute ratio of variation (MAROV) value. A brief description of the parameters is provided in Table 3.

	Wick soil				Hodnet soil			
	Pesticide 1		Pesticide 2		Pesticide 1		Pesticide 2	
	Parameter	MAROV	Parameter	MAROV	Parameter	MAROV	Parameter	MAROV
1	DEG	8.16	FREUND	22.2	DEG	3.10	TPORV	6.68
2	FREUND	4.55	ZKD	12.1	TPORV	2.70	ZN	2.74
3	ZKD	4.50	DEG	12.0	TRESP	1.77	XMPOR	2.27
4	TRESP	3.49	KSM	7.00	FREUND	1.35	FREUND	2.07
5	XMPOR	2.47	TPORV	5.90	KSM	1.25	KSM	1.62
6	GAMMA	2.36	ZN	5.62	XMPOR	0.94	ASCALE	1.50
7	ANNTAV	1.82	GAMMA	3.68	ZN	0.82	DEG	1.22
8	ZLAMB	0.83	TRESP	3.37	ASCALE	0.69	DIFF	0.83
9	ANNAMP	0.57	ANNTAV	2.23	ANNTAV	0.60	TRESP	0.72
10	TPORV	0.52	ZLAMB	1.45	ZLAMB	0.46	ZKD	0.63
11	EXPB	0.51	RINTEN	0.95	ROOTMAX	0.37	KSATMIN	0.55
12	KSM	0.39	XMPOR	0.95	WILT	0.36	GAMMA	0.45
13	ZALP	0.28	ASCALE	0.87	RPIN	0.32	ANNTAV	0.41
14	ASCALE	0.25	CTEN	0.87	DIFF	0.30	ZLAMB	0.34
15	RINTEN	0.23	EXPB	0.86	KSATMIN	0.27	ROOTMAX	0.29

influence as compared with the sandy loam, especially for the scenario describing the leaching of Pesticide 2. The parameter that most influenced the prediction of pesticide losses by MACRO for the two clay loam scenarios was TPORV, the soil water content measured at zero tension. Other parameters that most influence predictions of pesticide losses in the Hodnet soil included the pore size distribution factor for macropores (ZN), the hydraulic conductivity, and the water content at the micropore–macropore boundary (KSM and XMPOR), respectively. The first parameter related to sorption or degradation, the Freundlich exponent, came fourth in the ranking.

Broad results for the four scenarios are in line with

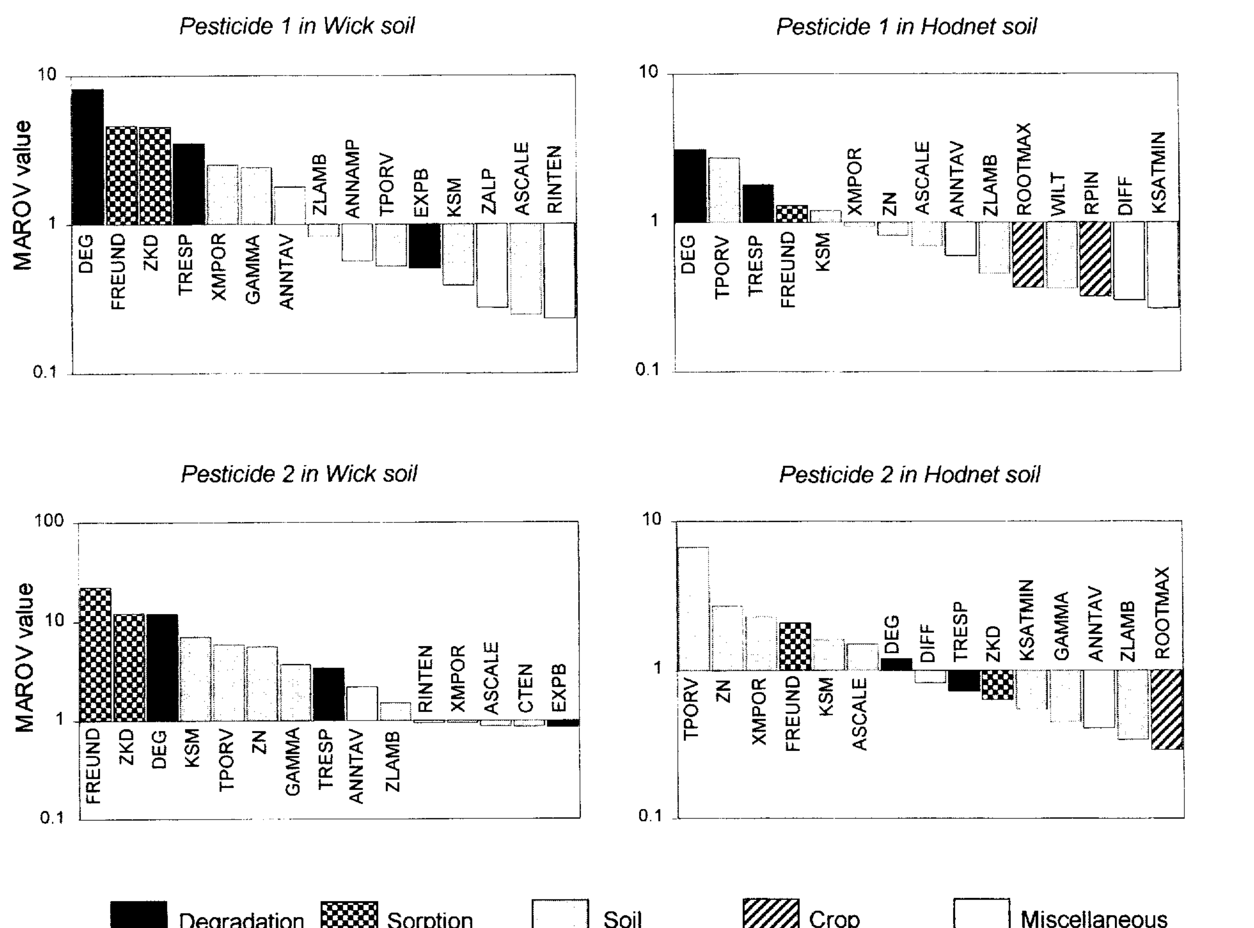

Fig. 3. Classification into broad classes of the 15 most influential parameters for predictions of pesticide losses for the four scenarios (one-at-a-time approach). Parameters are classified by decreasing influence according to their maximum absolute ratio of variation (MAROV) value.

Table 8. Classification of MACRO input parameters according to their influence on the prediction of pesticide losses at a 1-m depth (Monte Carlo approach). Parameters are classified by decreasing influence according to their standardized rank regression coefficient (SRRC) value. A brief description of the parameters is provided in Table 3.

	Wick soil				Hodnet soil			
	Pesticide 1		Pesticide 2		Pesticide 1		Pesticide 2	
	Parameter	SRRC	Parameter	SRRC	Parameter	SRRC	Parameter	SRRC
1	DEG	−0.648	FREUND	0.523	DEG	−0.730	ASCALE	0.463
2	ZKD	−0.483	ZKD	−0.484	TRESP	0.331	KSM	−0.345
3	FREUND	0.292	DEG	−0.479	KSM	−0.268	ZN	−0.294
4	TRESP	0.287	KSM	−0.210	ZN	−0.208	DEG	−0.286
5	ANNTAV	−0.144	ZN	−0.210	ASCALE	0.179	FREUND	0.261
6	ZLAMB	0.104	TRESP	0.182	FREUND	0.170	DIFF	−0.235
7	FSTAR†	−0.060	ANNTAV	−0.110	TPORV	−0.167	ZKD	−0.214
8	EXPB	0.055	ZLAMB	−0.097	ZLAMB	−0.162	TPORV	−0.205
9	WILT	−0.052	ASCALE	0.082	ANNTAV	−0.114	ZLAMB	−0.131
10	XMPOR	−0.048	EXPB	0.082	DIFF	−0.100	TRESP	0.110
11	ZFINT	−0.047	KSATMIN	0.075	ZKD	−0.092	FRACMAC	−0.099
12	GAMMA	−0.036	RINTEN	0.071	KSATMIN	0.059	RINTEN	0.089
13	ZM	−0.035	GAMMA	−0.068	XMPOR	0.051	CTEN	−0.082
14	ZMIX	−0.034	FRACMAC	−0.066	ANNAMP	0.050	KSATMIN	0.081
15	KSM	0.030	ROOTINIT	0.063	CTEN	−0.050	XMPOR	0.081

† FSTAR was not included in the one-at-a-time sensitivity analysis.

those expected. The large influence of parameters related to the description of the soil hydrology and in particular to the definition of the micropore–macropore region has previously been reported for a heavy clay soil (Jarvis, 1991). In soils that are prone to preferential flow, parameters that determine the precise extent of this will have a significant sensitivity for pesticide losses. It is also known that preferential flow is relatively more important in determining leaching of more strongly sorbed chemicals (Larsson and Jarvis, 2000). In contrast, varying hydraulic parameters in coarse-textured soils where MACRO simulates little or no preferential flow will have a much smaller impact on pesticide losses.

Results for the Monte Carlo Approach

A total of 250 runs were carried out for each of the four scenarios. The 15 input parameters with the largest standardized rank regression coefficient are presented in Table 8. There was a fairly good agreement between the results from the two investigation methods for the first two scenarios, with a dominance of the parameters related to sorption and degradation for the scenarios involving the sandy loam. In contrast to the results from the one-at-a-time sensitivity analysis for the Hodnet soil, the influence of hydrological input parameters on the prediction of pesticide losses was found to be less evident with the Monte Carlo investigations for the third scenario (Pesticide 1 on Hodnet soil). It is often the case that sensitivity analysis methods that are conceptually different yield different rankings, although the ranking for the top several sensitive parameters is usually consistent (Hamby, 1995). A number of reasons can be proposed to explain the differences in the top parameters between the two methods for the third scenario. First, this might be attributed to the use of probability density functions that did not match the variation of the input parameters in the one-at-a-time sensitivity analysis. Second, parameters were all varied at the same time in the Monte Carlo approach compared with the single parameter variation in the one-at-a-time sensitivity analysis. Third, the derivation of the SRRC coefficients in the Monte Carlo approach relies on a linear regression between ranked values for pesticide losses and ranked values for input parameters. Results for standardized data clearly showed that the system considered was nonlinear (r^2 = 0.68–0.90 for the four scenarios). It is thus questionable whether the investigation of the sensitivity of nonlinear models (such as most deterministic environmental and ecological models) using an approach based on Monte Carlo sampling and multiple linear regressions is appropriate. The rank transformation that was applied to the data improved the fit of the multiple linear regression (r^2 = 0.92–0.95 for the four scenarios). Still, deviations from linearity might introduce some uncertainty into the ranking of input parameters.

The hydrological description in MACRO uses Richards' equation. In both the one-at-a-time and Monte Carlo approaches, parameters related to the description of the water retention and hydraulic conductivity curves (CTEN, KSM, TPORV, XMPOR, ZLAMB, ZM, and ZN) were varied independently. This could lead to unreasonable combinations of these parameters, which may subsequently result in unrealistic water hydrology curves. Figures 4 and 5 provide a comparison of the variation of the water retention and hydraulic conductivity curves using the two different approaches for the first horizons of the two soils. In the one-at-a-time sensitivity analysis, most of the variations applied resulted in a relatively small deviation of the curves from the base-case scenarios. The maximum spread of the 250 water retention and hydraulic conductivity curves generated from the random sampling into probability distribution functions for each individual parameter approximately corresponded to the maximum deviations obtained in the one-at-a-time sensitivity analyses. All curves resulting from the independent sampling of parameter values were considered realistic although the assessment is somewhat subjective. A visual examination of Fig. 4 suggests that the base-case water retention

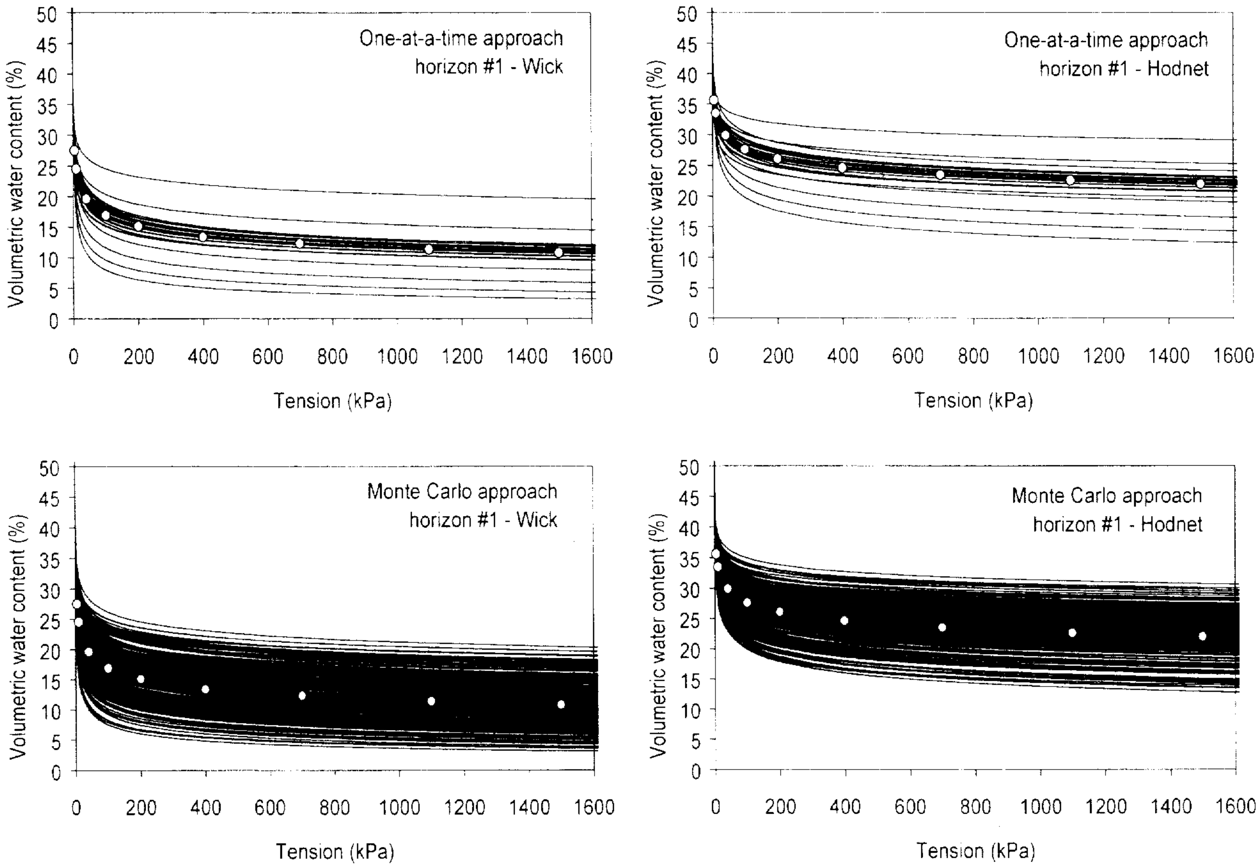

Fig. 4. Variations of the water retention curves in the one-at-a-time (top two charts) and Monte Carlo (bottom two charts) approaches. Water retention curves generated in the sensitivity analyses (black lines) are compared with those from the base-case scenarios (open circles). All curves are modeled using the Brooks and Corey equation implemented in MACRO.

curves (open circles) were central estimates in the populations of water retention curves resulting from Monte Carlo sampling (black lines). Similar conclusions could be drawn from the examination of the variation of the water retention curves for the other horizons of the two soils (data not shown). Hydraulic conductivities generated by Monte Carlo sampling were log-normally distributed except in the region of the curve inflection where Weibull distributions fitted the data better. It is therefore possible that the discrepancies in the results between the one-at-a-time and Monte Carlo approaches may be attributed to some extent to the differences in representation of the variation in the water retention curves.

Although the primary aim of the Monte Carlo approach we followed was to investigate the sensitivity of MACRO, results can be used as a first step assessment of the uncertainty associated with the modeling. This assessment was made possible because parameters were varied within a range that reflected their uncertainty. Box plots showing the distribution of the predictions for pesticide losses for the four scenarios are presented in Fig. 6. The maximum variation in the prediction of pesticide losses by MACRO was observed for Pesticide 1 on the Wick scenario. Losses were predicted to vary from 0 to 340 g ha^{-1}. Focusing on extremes is inappropriate for the Monte Carlo assessment of uncertainty since the extreme upper tail of the distribution is data poor and is characterized by high uncertainty (Wolt, 1999). Predictions related to the largest losses were only attributed to a few runs that most probably combined extreme values of input parameters. For the scenario involving Pesticide 2 and the Wick soil, the last five of 250 runs contributed to the increase of the maximum predicted losses from 110 to 250 g ha^{-1}. Less uncertainty is associated with the middle part of the distributions and indicators such as the 25th and 75th percentile are therefore more appropriate to characterize the uncertainty. Coefficients of variation (CVs) for pesticide losses ranged from 60% (Pesticide 1 on Hodnet) to 150% (Pesticide 2 on Wick) and were in sharp contrast with CVs for the prediction of percolation volumes (6–7%, data not shown). The largest uncertainty in the prediction of pesticide losses was related to the scenario for which the smallest losses were predicted (Table 5). The first-step probabilistic analyses considered the uncertainty originating from the uncertainty in the attribution of values to input parameters. The predictive uncertainty resulting from the inability of the model to represent reality accurately even when adequate input data are supplied ("model error") was not taken into account. Uncertainties for a large number of input parameters were considered in this study. It is likely that most probabilistic risk assessments will limit variation to the most

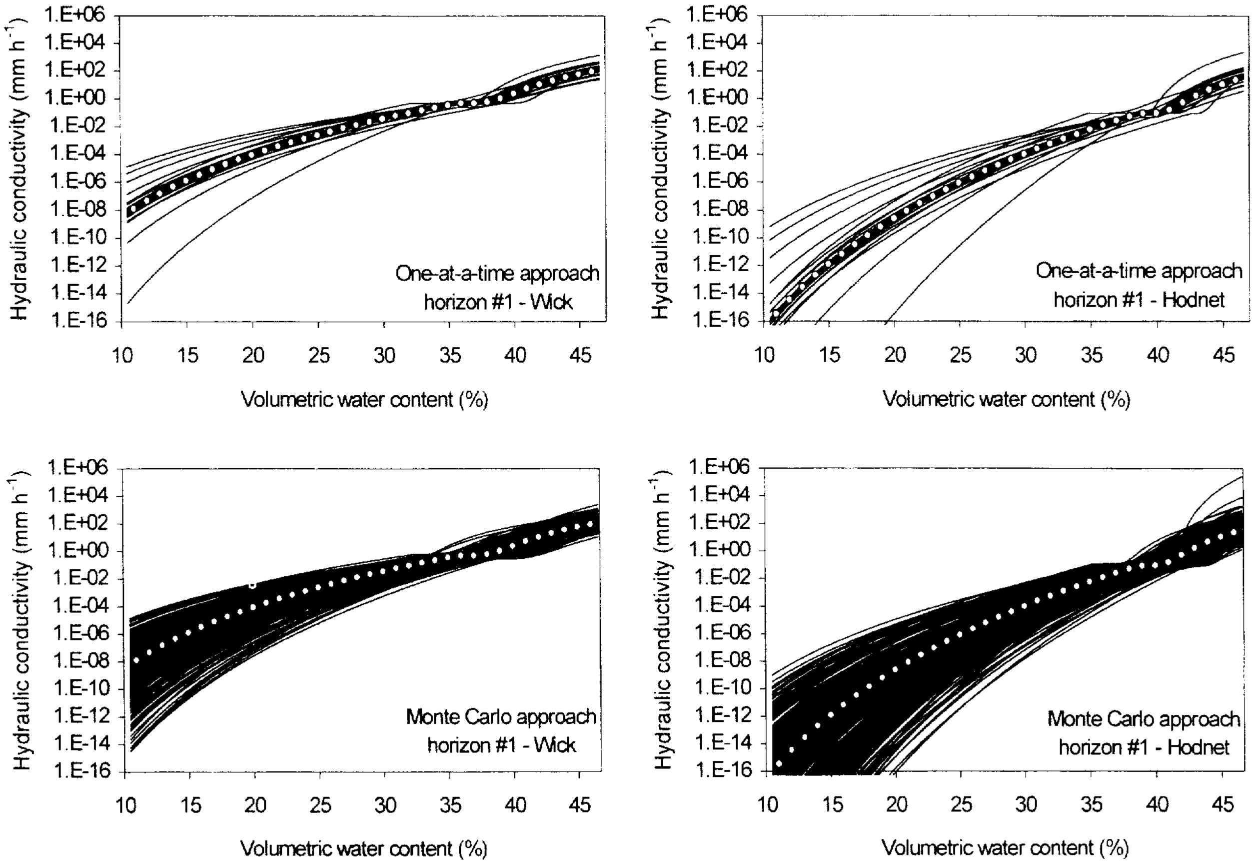

Fig. 5. Variations of the hydraulic conductivity curves in the one-at-a-time (top two charts) and Monte Carlo (bottom two charts) approaches. Hydraulic conductivity retention curves generated in the sensitivity analyses (black lines) are compared with those from the base-case scenarios (open circles).

sensitive parameters as identified in this study and that the resulting variability in model predictions will be less.

Implications for Modeling with MACRO

A total of four scenarios was used to rank input parameters with respect to their influence on the predictions by MACRO of accumulated percolation volumes and pesticide losses. Although it is recognized that results of any sensitivity analysis are scenario-specific (Ferreira et al., 1995), the use of four contrasting scenarios is a clear improvement over sensitivity analyses carried out for a single scenario. Within the limits of the

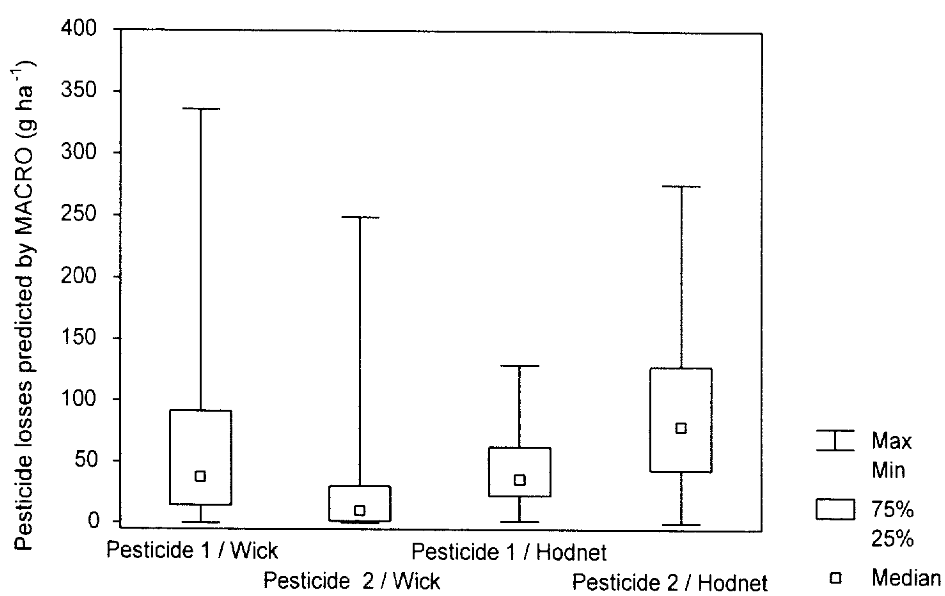

Fig. 6. Box plots describing the distributions of predictions for pesticide losses for the four scenarios (Monte Carlo approach).

scenarios and assumptions of the sensitivity analysis, parameters related to sorption and degradation processes were found to have the largest influence on predictions of pesticide losses by MACRO, especially for the coarse-textured soil. The description of pesticide sorption and degradation in MACRO is relatively simple because of the potential for complex interactions between these processes and mass transfer between the four model compartments (micropores–macropores and solid–liquid phases). For example, sorption equilibrium is assumed to be instantaneous and fixed and degradation is characterized as a single, first-order process. Reports in the literature suggest that these simplifying assumptions are not universally valid (Boesten, 2000) and the descriptions of these processes in MACRO should be critically reviewed in cases where degradation and sorption parameters are dominant in determining leaching.

The Hodnet soil has been shown to have a significant component of preferential flow (Beulke et al., 1999) and here there was a greater influence of parameters related to the description of soil hydrology, particularly for the more strongly sorbed compound. Values for several of the hydraulic parameters are difficult to obtain independently and expert judgement is often required for their derivation. Examples include the pore size distribution factor for macropores (ZN) and the hydraulic conductivity and water content at the micropore–macropore boundary (KSM and XMPOR, respectively). This difficulty potentially limits the predictive use of the model. Future research should address the derivation of independent experimental procedures to assess adequate values for these parameters or the use of alternative parameters more accessible to an experimental estimation. In common with other pesticide leaching models, the evaluations of MACRO reported in the literature have focused on the application of the sum of subroutines to experimental data rather than on any critical review of individual process descriptions. Examination of the individual components of the model would be useful for further refinement of specific subroutines, particularly in those instances where parameters have been shown to be particularly sensitive.

Detailed ranking of input parameters (Tables 6 and 7) is expected to have a number of applications in modeling with MACRO. First, the information can be used to guide parameterization efforts and identify those parameters whose values require the most (or the least) time and financial resources for their determination. Second, the information can assist when selecting parameters for adjustment when calibrating the model to experimental data, either manually or by inverse modeling. The third application of these results relates to probabilistic modeling. The probabilistic approach to modeling recognizes the uncertainty associated with input parameters and aims at propagating it through the modeling process to estimate the uncertainty associated with model predictions. The information on the sensitivity of MACRO derived here can be combined with information on the uncertainty associated with input parameters to select those few parameters that need to be considered within a probabilistic framework (Labieniec et al., 1997). For simulation of a scenario significantly different from those presented here (e.g., use of a different bottom boundary condition, simulation of losses of a different nature, application in the spring rather than the winter), it is recommended that a rapid sensitivity analysis is carried out to confirm those parameters that most influence model predictions. This might concentrate on, say, the 10 to 15 most sensitive parameters identified in the broad analysis presented here and those extra parameters resulting from the simulation of the new scenario.

Given the sensitivities reported in this study and the large uncertainties associated with some input parameters (either specific to MACRO or not), it appears desirable to consider uncertainty within the modeling carried out for pesticide registration. A probabilistic approach would provide improved transparency in the risk assessment procedure and help to attach confidence levels to model predictions for pesticide losses.

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