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CALIBRATION OF PESTICIDE LEACHING MODELS

Cranfield Centre for EcoChemistry

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EXECUTIVE SUMMARY

Complex deterministic models are being used within the context of pesticide registration to assess the potential for crop protection products to impact on the environment. Although calibration is in many ways at the heart of pesticide fate modelling, it has received little attention in the past. Sensitivity analyses were carried out for the four main leaching models used for pesticide registration in Europe (PELMO, PRZM, PESTLA and MACRO) using four different leaching scenarios and two approaches to sensitivity assessment (one-at-a-time and Monte Carlo sensitivity analyses). Also, an inverse modelling approach was used to estimate values for sorption and degradation parameters from leaching data for seven lysimeters using the PESTRAS model.

The overall conclusions of the PhD can be summarised as follows:

1. Sensitivity analyses for the four leaching models mainly used for pesticide registration in Europe demonstrated that predictions for pesticide loss are most sensitive to parameters related to sorption and degradation. In a small number of scenarios, hydrological parameters were found to also have a large influence on predictions for pesticide loss.
2. Sensitivity analysis proved to be an effective approach not only for ranking parameters according to their influence on model predictions, but also for investigating model behaviour in a more general context. However, the research questioned the robustness of the Monte Carlo approach to sensitivity analysis as issues of replicability were uncovered.
3. Inverse modelling exercises demonstrated that non-uniqueness is likely to be widespread in the calibration of pesticide leaching models. Correlation between parameters within the modelling, such as that between sorption and degradation parameters when predicting pesticide leaching, may prevent the robust derivation of values through an inverse modelling approach. Depending on the calibration system considered, these parameters may act as fitting variables and integrate inaccuracies, uncertainties and limitations associated with experimental data, modelling and calibration.
4. A special implementation of error surface analysis termed lattice modelling was proposed in the PhD as an efficient technique to i) assess the likely extent of non-uniqueness issues in the calibration of pesticide leaching models; and, ii) replace traditional parameter estimation procedures where non-uniqueness is expected.

Care should be exercised when assessing the results obtained by both modelling and inverse modelling studies. Suggestions to improve the reliability in the calibration of pesticide leaching models have been proposed.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to Dr Colin Brown for having supervised the present PhD and, more generally, for allowing me to develop work in higher tier modelling techniques within Cranfield Centre for EcoChemistry. His helpful suggestions for improving earlier versions of the papers presented in this thesis, his attention to detail, rigor and honesty have been much appreciated. My thanks also go to my colleague Dr Sabine Beulke for her contribution to this PhD in the form of collaborative work on inverse modelling and informal discussions on multiple aspects of pesticide fate modelling and model calibration.

Most of the investigations reported in the present document were undertaken within the scope of research projects funded by the Pesticides Safety Directorate through the UK Department for Environment, Food and Rural Affairs (formerly the Ministry of Agriculture, Fisheries and Food) or by BASF AG. The funding of this research is gratefully acknowledged.

My wife Hélène has been supportive of this work right from the start. Her understanding and moral support during the many evenings and weekends I spent at the computer at home or in the office have been very much appreciated. This work is dedicated to her and to our son Elliott.

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ACRONYMS USED

BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
CAMASE	Concerted Action for the development and testing of quantitative Methods for research and Agricultural Systems and the Environment
CMLS	Chemical Movement in Layered Soils
DAT	Days After Treatment
DEFRA	Department for Environment, Food and Rural Affairs
DOS	Disk Operated System
EC	European Commission
ECOFRAM	Ecological Committee On FIFRA Risk Assessment Methods
EU	European Union
EUPRA	EUropean workshop on Probabilistic Risk Assessment for the environmental impacts of plant protection products
FAO	Food and Agriculture Organization
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FOCUS	FOrum for the Coordination of pesticide fate models and their USe
GA	Genetic Algorithm
GC-MS	Gas Chromatography – Mass Spectrometry
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems
GLUE	Generalized Likelihood Uncertainty Estimation
IUPAC	International Union of Pure and Applied Chemistry
LEACHP	Leaching Estimation And CHemistry model - Pesticides
LHS	Latin Hypercube Sampling
MAROV	Maximum Absolute Ratio Of Variation
MOUSE	Method Of Underground Solute Evaluation
PEARL	Pesticide Estimation Assessment at the Regional and Local scale
PELMO	PEsticide Leaching MOdel
PEST	Parameter ESTimation
PESTLA	PESTicide Leaching and Accumulation
PESTRAS	PESticide TRansport ASsessment

PET	Potential Evapotranspiration
PRZM	Pesticide Root Zone Model
PSD	Pesticides Safety Directorate
RORASC	ROtated RAndom SCan
RZWQM	Root Zone Water Quality Model
SENSAN	SENSitivity ANalysis
SRRC	Standardised Rank Regression Coefficient
SUFI	Sequential Uncertainty domain parameter FItting
UNCSAM	UNCertainty analysis by Monte Carlo SAMpling technique
US EPA	United States Environmental Protection Agency

Chapter 1

INTRODUCTION

LEACHING MODELS AND PESTICIDE REGISTRATION IN THE EU

The increasing use of crop protection products in agriculture over the last fifty years has been considered a major potential threat to groundwater resources for a long time (Dorst, 1965). Pesticides have been repeatedly found in aquifers underlying regions where agricultural activities are predominant (IUPAC, 1987; US EPA, 1992), albeit usually at concentrations unlikely to cause environmental or health concerns (Cohen, 1996; Environment Agency, 2000). This occurrence demonstrates the need for a rational use of pesticides in relation to their potential impact on environmental resources and human health.

The risk of a compound impacting on the environment is typically assessed through a range of approaches (Russell, 1995), ranging from simple laboratory determinations (US EPA, 2002) through to advanced simulation modelling (Ritter *et al.*, 2000; Campbell *et al.*, 2000; Bartell *et al.*, 2000; Brown *et al.*, 2001). If simple tests indicate a potential for leaching to depth, then experimental studies are carried out under conditions increasingly resembling those prevailing in the field. The experimental approach to the assessment of pesticide leaching however suffers from a number of limitations, including the time required to perform field studies (typically two to three years), the site-specific nature of the results and the cost involved. In comparison, the use of mathematical models simulating pesticide leaching is cost- and time-effective and does not rely on rainfall and other environmental factors to produce results of interest. Furthermore, modelling offers the possibility of encompassing the variability in weather conditions through the use of long-term meteorological data series and may offer extrapolation capabilities to other climates, soil and cropping practices. These benefits have led to the development of a large number of models capable of simulating leaching of

pesticides in soils in the last twenty years or so, contrasting in their complexity, input requirements and intended use (Mills & Leonard, 1984; Carsel *et al.*, 1985; Rao *et al.*, 1985; Jury *et al.*, 1986; Nofziger & Hornsby, 1986; Jarvis *et al.*, 1991; Hutson & Wagenet, 1992; Knisel *et al.*, 1992; RZWQM team, 1992; Grochulska & Kladivko, 1994; Tiktak *et al.*, 2000).

Although models were initially developed within a research context, they are now widely used for assessing the potential transfer of pesticide to groundwater resources within the pesticide registration process (Travis, 2000). Modelling has now become a cornerstone in pesticide registration and four models are mainly used in Europe to assess the potential for a compound to impact on groundwater (FOCUS, 2000). These are: the PEsticide Leaching MOdel (PELMO; Jene, 1998), the Pesticide Root Zone Model (PRZM; Carsel *et al.*, 1998), the Pesticide Estimation Assessment at the Regional and Local scale model (PEARL; Tiktak *et al.*, 2000) and the preferential flow model MACRO (Jarvis & Larsson, 1998). PELMO and PRZM are similar models which implement a simple description of hydrology based on a simple 'tipping-bucket' approach where water will be transferred from one layer to the next only if the maximum capacity of the layer to hold water is exceeded. Both models simulate leaching of pesticides to depth and losses of product by erosion, run-off and volatilisation. PEARL resulted from the recent combination of PESTLA (van den Berg & Boesten, 1999) and PESTRAS (Tiktak *et al.*, 1994), two pesticide leaching models developed and used for pesticide registration in the Netherlands. PEARL implements a description of the water flow based on the Richards' equation while solute transport is simulated using the convection-dispersion equation. The model is appropriate for simulating the interaction between the unsaturated zone and the upper groundwater. MACRO is the only one of the four models which can simulate the rapid transfer of water and solutes through the soil profile resulting from preferential flow phenomena (Brown *et al.*, 2000). The total soil porosity is divided into two flow domains (macropores and micropores), each characterised by a flow rate and solute concentration. Soil water flow and solute transport in the micropores is modelled using Richards' equation and the convection-dispersion equation, respectively, whilst fluxes in the macropores are based on a simpler capacitance-type

approach with mass flow. The four models describe pesticide degradation using a first-order decay equation and sorption of pesticides to soil is simulated using the Freundlich equation.

The extensive use of these models within the context of the placement of crop protection products on the market means that all parties involved need to have confidence in the ability of these models to simulate and predict the fate of pesticides in the environment. This was recognised formally by the EU directive 95/36/EC which states that "models used for the estimation of predicted environmental concentrations must […], where possible, be reliably validated with measurements carried out under circumstances relevant for the use of the model" (EC, 1995). The four pesticide leaching models used for pesticide registration in Europe have been evaluated in a number of 'validation' exercises in the past (Pennell *et al.*, 1990; Bergström & Jarvis, 1994; Walker *et al.*, 1995; Klein *et al.*, 1997; Vanclooster *et al.*, 2000). All these evaluation studies relied, in some form or another, on calibration of pesticide leaching models against experimental data.

MODEL CALIBRATION IN PESTICIDE FATE MODELLING

Calibration consists of the iterative adjustment of input parameters of a model to provide an 'acceptable' fit between model predictions and the experimental data. Within pesticide fate modelling, calibration is typically used i) to test the ability of pesticide leaching models to provide an adequate reflection of pesticide behaviour in the field (model evaluation); ii) to help in the parameterisation of these complex models (model parameterisation); iii) to establish the basis for subsequent extrapolation to different environmental conditions (extrapolation); and, iv) to estimate appropriate values for selected parameters (parameter estimation or inverse modelling approach). The latter use is likely to develop in pesticide fate modelling in the near future since it has been proposed that calibration of a pesticide leaching models against field data could enable the derivation of values for sorption and degradation parameters representative of field conditions (Gottesbüren, 1998).

Sorption and degradation properties are typically derived in the laboratory, but there is a debate as to whether these values are useful to simulate field behaviour (Beulke *et al.*, 2000). Sorption and degradation parameters play a particular role in the registration process as they often provide a first estimate of the environmental fate of pesticides. The estimation of sorption and degradation values through calibration of a pesticide leaching model is commonly referred to as 'inverse modelling' although it should be noted that this term is more general and designates any parameter estimation.

The calibration of pesticide leaching models has received little attention in the past although it is clearly an important aspect in the modelling of the fate of pesticides and advanced techniques for model calibration have been used in other fields of modelling. This thesis presents work undertaken by the candidate in the closely related fields of i) the sensitivity of pesticide leaching models; and, ii) the calibration of these models. Investigations concentrated on the main models used for pesticide registration in Europe.

AIMS AND OBJECTIVES

The overall aims of the PhD were to advance the scientific understanding in the calibration of pesticide leaching models and to assess the confidence that should be placed in modelling and calibration results. The objectives of this work were i) to investigate the sensitivity of pesticide leaching models; ii) to critically evaluate existing procedures for their calibration; and, iii) to develop alternative procedures for the calibration of pesticide leaching models where significant shortcomings in current approaches were identified. The present work is one of the first contributions to the specific study of sensitivity and calibration aspects for the main pesticide leaching models.

FORMAT OF PRESENTATION

The thesis is presented in the form of a collection of stand alone papers organised in chapters, which between them, address the aims and objectives described above.

Chapter 2 is a critical review of calibration activities in pesticide fate modelling. The chapter first reviews specific uses of calibration in studying the fate of crop protection products and in their registration. Issues associated with the calibration of pesticide leaching models are discussed in detail. These include: the qualitative and quantitative data requirements for calibration; the selection of an adequate model and input parameters to be varied in the calibration; differences in approaches to calibration; difficulties associated with the comparison between model output and experimental data; and, potential pitfalls associated with model calibration and parameter estimation.

Chapter 3 reports on sensitivity analyses which were carried out for PELMO, PRZM, PESTLA and MACRO. A one-at-a-time approach was used to identify those parameters which most influence model predictions for volumes of percolation water and pesticide loss via leaching. Four scenarios comprising different soils and pesticides were considered in the analysis to reflect the influence of varying modelling conditions on sensitivity results. Information on the sensitivity of models plays a key role in the selection of parameters to be varied in a calibration exercise.

Chapter 4 provides a detailed analysis of the results of sensitivity analyses carried out for the preferential flow model MACRO. Two approaches were used: a one-at-a-time approach similar to that used in Chapter 3 and a method based on Monte Carlo sampling. The two methodologies are compared and recommendations for the study of the sensitivity of pesticide leaching models are proposed. The chapter also provides an assessment of the uncertainty in MACRO predictions resulting from that in input parameters.

Chapter 5 presents an application of the inverse modelling approach to estimate sorption and degradation parameters from leaching data for seven lysimeters. The potential benefits gained from the use of automated calibration techniques in pesticide fate modelling are presented.

Chapter 6 reports on additional investigations undertaken on three of the seven lysimeter datasets presented in Chapter 5. The research was intended to assess the confidence that should be attributed to results from parameter estimation exercises. Investigations concentrated on the influence on calibration results of i) the attribution of different values to parameters not varied in the calibration; and, ii) the supply of different starting values to the inverse modelling package. A methodology is proposed to identify those situations where non-uniqueness in calibration is likely to occur. The proposed procedure is an efficient alternative to the inverse modelling approach for estimating sorption and degradation parameters from field data.

Chapter 7 assesses the implications of the findings reported in the preceding chapters for pesticide registration and more generally, for the calibration of pesticide leaching models. Perspectives with regard to the future of model calibration are discussed, research priorities are identified and conclusions are drawn.

Chapters 2 to 6 of the present thesis have been prepared as stand-alone papers for submission to international peer-reviewed journals while Chapter 7 is intended to form the basis of a future conference paper. The status of the different papers with regard to the publication process is presented in Table 1-1. Although submission of the papers to different journals meant that the style of the manuscripts differed, all these documents have been reworked to provide a consistent style across this PhD thesis. For those papers which have been published, copyright rests with the publishers.

A significant number of tables in Chapters 2 to 6 of this thesis are large and span over two pages or more. It has therefore been decided to regroup tables and figures at the end of these chapters to improve readability.

CONTEXT AND DISCLOSURE

The work in this thesis was undertaken as a part-time staff candidate while working as a research scientist and then senior research scientist at Cranfield Centre for EcoChemistry in Silsoe. The body of work on sensitivity analysis and model calibration was developed over four years through research projects undertaken for the Pesticides Safety Directorate via the UK Department for Environment, Food and Rural Affairs (projects PL0528, PL0532, PL0539) and the agrochemical company BASF AG (project JF4198S). The work presented in Chapters 6 and 7 resulted from a personal research initiative outside the scope of funded projects.

All the papers included in the present document have joint authorship reflecting the composition of the modelling team at Cranfield Centre for EcoChemistry. All five papers have been written by the candidate as leading author. However, it should also be noted that these papers have gained in quality through suggestions and editing from the co-authors, and especially from Colin Brown who ensured that the reporting of the research conducted was meeting highest quality standards. Chapters 2 and 4 which are in press and published, respectively, have also benefited from comments of referees as part of the review process. The definition of scenarios and the attribution of variation ranges reported in Chapters 3 and 4 benefited from a strong input from Colin Brown. The lysimeter data supporting the work presented in Chapters 5 and 6 were provided by Bernd Gottesbüren (BASF AG) and initial simulations with PESTRAS were undertaken by Sabine Beulke.

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Table 1-1. Publication status of the five papers presented in the PhD thesis.

The papers are presented in logical rather than chronological order.

Authors	Paper title	Journal	Status	Corresponding chapter in the thesis
Dubus I.G., Beulke S. & Brown C.D.	Calibration of pesticide leaching models: critical review and guidance for reporting	Pest Management Science	In press (paper accepted for publication in April 2002)	Chapter 2
Dubus I.G., Brown C.D. & Beulke S.	Sensitivity analyses for leaching models used for pesticide registration in Europe	Pest Management Science	In press (paper accepted for publication in May 2002)	Chapter 3
Dubus I.G. & Brown C.D.	Sensitivity and first-step uncertainty analyses for the preferential flow model MACRO	Journal of Environmental Quality	Published (volume 31, pages 227 to 240)	Chapter 4
Dubus I.G., Beulke S., Brown C.D. & Gottesbüren B.	Inverse modelling for estimating sorption and degradation parameters for pesticides. Part 1: datasets and initial calibrations	Soil Science Society of America Journal	Submitted in May 2002	Chapter 5
Dubus I.G., Brown C.D. & Beulke S.	Inverse modelling for estimating sorption and degradation parameters for pesticides. Part 2: calibration non-uniqueness	Soil Science Society of America Journal	Submitted in May 2002	Chapter 6

Chapter 2

CALIBRATION OF PESTICIDE LEACHING MODELS: CRITICAL REVIEW AND GUIDANCE FOR REPORTING

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ABSTRACT

Calibration of pesticide leaching models may be undertaken to evaluate the ability of models to simulate experimental data, to assist in their parameterisation where values for input parameters are difficult to determine experimentally, to determine values for specific model inputs (*e.g.* sorption and degradation parameters) and to allow extrapolations to be carried out. Although calibration of leaching models is a critical phase in the assessment of pesticide exposure, the lack of guidance means that calibration procedures default to the modeller. This may result in different calibration and extrapolation results for different individuals depending on procedures used and thus may influence decisions regarding the placement of crop protection products on the market. A number of issues are discussed in the paper including: data requirements and assessment of data quality, the selection of a model and parameters for performing calibration, the use of automated calibration techniques as opposed to more traditional trial-and-error approaches, difficulties in the comparison of simulated and measured data, differences in calibration procedures and the assessment of parameter values derived by calibration. Guidelines for the reporting of calibration activities within the scope of pesticide registration are proposed.

Dubus I.G., Beulke S. & Brown C.D. Calibration of pesticide leaching models: critical review and guidance for reporting. *Pest Management Science*, in press.

INTRODUCTION

Environmental exposure to crop protection products is traditionally assessed using a range of tools, including laboratory, lysimeter and field experiments and the use of computer simulation models. Although the use of computer models in pesticide registration is an attractive option in terms of temporal, financial and manpower resources when compared to experimentation (Gustafson, 1995), modelling is not sustainable on its own and experimental work is necessary. There is an intimate although complex relationship between models and experimental data. Extrapolation using predictive models may act as a substitute for field studies since experimental investigation of the fate of crop protection products for multiple locations and climatic conditions is impractical. However, experimental data are essential for model development, for evaluating the accuracy of models in the description of field behaviour and thus for assessing the confidence that should be placed in model predictions. Calibration of fate models against experimental data is hence often at the heart of exposure assessment for crop protection products, especially at higher tiers.

Despite the complexity of pesticide leaching models in use and the large number of model input parameters that could be varied, the required activities for calibration are often given little consideration (Janssen & Heuberger, 1995). The calibration process is left to the discretion of the modeller and thus an *ad hoc* approach is adopted. There have been numerous calls for the development of guidelines in relation to modelling (FOCUS, 1995; Gustafson, 1995; Vanclooster *et al.*, 2000) to decrease the uncertainty and the large user-subjectivity associated with the use of pesticide leaching models (Brown *et al.*, 1996; Vanclooster *et al.*, 2000). Codes of "Good Modelling Practice" have been proposed by Görlitz (1993) and Estes & Coody (1994). Good Modelling Practices were defined as "the development, maintenance, distribution and use of computer simulation models whereby the integrity of the model, its various improvements and utilisation is assured" (Estes & Coody, 1994). These documents provide a general framework for ensuring the

quality, consistency and integrity of the models (FOCUS, 1995), but do not provide guidelines on either the model parameterisation *per se* or on calibration.

The development of detailed modelling guidelines that are broadly applicable is a difficult task given the heterogeneity of modelling situations. Resseler and coauthors (1997) have issued recommendations for performing modelling studies for registration purposes, but these are mainly relevant to the German registration context. CAMASE, an EU-funded workgroup, have issued general guidelines for modelling which cover the evaluation of models, sensitivity and uncertainty analyses and calibration (CAMASE, 1995). The guidance for calibration was intended to be applicable to a large range of environmental models and this resulted in the derivation of general concepts rather than specific guidelines. More recently, the FIFRA Environmental Model Validation Task Force has issued a report containing guidance information for calibrating leaching and run-off models (Jones & Russell, 2000). The report proposes some basic principles for calibration and identifies those parameters to be varied within the validation work undertaken by the Task Force. Although these two guidance documents for calibrating pesticide leaching models emphasise the need for a high quality report of calibration activities for improved transparency and reproducibility, detailed information that should be made available in calibration reports is not listed. Given the importance of written communication in the pesticide review process, the development of guidelines for reporting calibration activities appears desirable. The development of guidance for reporting is also expected to be useful in that indirect guidance for the performance of calibration can be suggested.

The present paper presents a critical review of the use of calibration and calibration procedures in pesticide fate modelling and proposes guidelines for reporting calibration activities within the context of pesticide registration.

THE USE OF CALIBRATION IN MODELLING THE ENVIRONMENTAL FATE OF PESTICIDES

Calibration of pesticide leaching models may be undertaken for a range of purposes which broadly fall under four categories: i) model parameterisation; ii) "validation" of models or of the use of models; iii) extrapolation; and iv) targeted parameter estimation.

Model Parameterisation

Most pesticide leaching models were initially developed as research tools to describe the fate of compounds in heavily instrumented field or laboratory experiments. For this reason, there has been little emphasis on the use of parameters which can be readily derived from easily measured data or on the development of procedures to support the parameterisation of a model for cases where few data are available. This has restricted the extensive use of detailed mechanistic models (Bergström, 1996). In some instances, the derivation of adequate values for input parameters relies on the fitting of a relationship to experimental data. Examples include the derivation of DT50 values from laboratory degradation data or the derivation of parameters of the van Genuchten or Brooks and Corey equations from water release data. Where such an independent assessment is not possible, parameter values may be attributed by calibration of the whole model ("indirect fitting"; Addiscott *et al.*, 1995) or by "expert judgement" where the experience and knowledge of the modeller prevail. Deterministic pesticide leaching models require a detailed set of theoretical parameters due to the highly complex and variable character of the natural soil-plant-atmosphere conditions which are simulated (Hanson *et al.*, 1999). Processes affecting the fate of pesticides in soil and water are numerous and difficult to characterise in terms of effective parameters. Some of the parameters integrated into the models cannot be easily measured or determined. Some authors have thus questioned the ability of pesticide leaching models to predict the fate of organic chemicals in the environment with acceptable accuracy and argue that a calibration

against measured data is always necessary to simulate the leaching of solutes (Hanson *et al.*, 1999). The requirement for calibration appears particularly important for preferential flow models (Bergström & Jarvis, 1994; Beulke *et al.*, 2001).

Model Testing or Model "Validation"

The testing of a model against experimental data is an essential activity that contributes to estimating the confidence that should be assigned to the predictions of the model. Such evaluations have been carried out for pesticide leaching models used for pesticide registration in Europe and the US (Pennell *et al.*, 1990; Bergström & Jarvis, 1994; Walker *et al.*, 1995; Klein *et al.*, 1997; Vanclooster *et al.*, 2000). The testing of the capacity of a model to describe or predict reality has often been referred to as "model validation" or "model verification" (Brooke & Matthiessen, 1991; Armstrong *et al.*, 1996; Watanabe & Takagi, 2000) even though it is demonstrated that complex environmental models cannot be proven or validated, but only tested and invalidated (Konikow & Bredehoeft, 1992; Oreskes *et al.*, 1994). The terminology used is misleading with regard to the confidence that should be assigned to the models and wording such as "model testing" or "model evaluation" is more appropriate (Konikow & Bredehoeft, 1992). Procedures for evaluating models have ranged from blind simulations where no calibration is carried out (Beulke *et al.*, 2001) to approaches where calibration is at the heart of the testing exercise (FOCUS, 1995). Although some authors evaluated a number of pesticide leaching models using predictive simulations only (Brown *et al.*, 1996; Klein *et al.*, 1997), the combination of blind and calibrated simulations in model evaluation has been the most common approach in recent years (Bergström & Jarvis, 1994; FOCUS, 1995; Thorsen *et al.*, 1998). Testing based on blind simulations will assess the accuracy of models where a potential use without calibration is expected. Blind simulations will provide an assessment of the model as well as the associated parameterisation, whereas controlled calibrated simulation can be considered as a truer test of the inherent capability of the model to represent field data. Loague (1992) suggested an evaluation approach in which a solute transport model is first calibrated against field

data from a specific period by adjusting input parameters until an acceptable fit is achieved and then run for a different time using the calibrated parameter set. The model is deemed validated if an "acceptable" fit is found between the model predictions and the experimental data for the second period (Kumar & Kanwar, 1997). However, a successful calibration of a model against experimental data could imply either that the model structure and the parameter values are both realistic, or that they are both unrealistic but compensate for one another (Kirchner *et al.*, 1996). Some authors consider that the only appropriate way of evaluating the accuracy and performance of a model is to attempt to predict the measured data with values for all parameters obtained independently (Brusseau, 1998). However, the parameterisation of complex pesticide leaching models often requires the use of expert opinion or pedotransfer functions to select values for some of the numerous input parameters required (Jarvis, 1999). A blind simulation will therefore not only test the model, but other aspects of the parameterisation as well, such as the data that were used to derive input values, the expert judgement of the modeller or the quality of the pedotransfer functions (Tiktak, 2000; Vanclooster & Boesten, 2000).

Extrapolation

Field and lysimeter experiments represent a major financial commitment for agrochemical companies wishing to register a new compound and modelling is commonly used to maximise the return on these studies. A possible approach is the use of experimental data to calibrate a leaching model and then use of the calibrated set of input parameters to make predictions for different environmental conditions (extrapolation). Extrapolations to radically different scenarios (*e.g.* between contrasting soil types or different climatic regions) are questionable given the uncertainty in the modelling and extrapolations are thus most often limited to small deviations from the calibrated set. A common form of extrapolation is the calibration of a model against field data for a number of years and then the running of the model for longer time series for the same site (Lorber & Offutt, 1986). The approach is considered of most interest when unusual weather conditions have been

experienced during a field study (Eckhardt & Wagenet, 1996). However, it has been demonstrated that the use of a single set of input parameters for different agricultural seasons might not lead to a good description of results over the entire experimental period (Loague, 1992; Brown *et al.*, 2000; Francaviglia *et al.*, 2000; Beulke *et al.*, 2001), especially under circumstances where droughts are experienced (Hanson *et al.*, 1999). Other examples of limited extrapolation are the use of an application rate different from that used in the calibration (Lorber & Offutt, 1986; Bergström, 1996) and the simulation of leaching deeper than the profile depth used during calibration (Loague *et al.*, 1995).

Two opposite views coexist with regard to the extrapolation of results from a calibrated set to different conditions. For some, successfully calibrating a model demonstrates its ability to simulate a specific set of conditions and allows one to extrapolate to other points in space and time (Durborow *et al.*, 2000). For others, the calibration of complex deterministic models tends to be specific to the conditions at the site for which experimental data were collected and no extrapolation should be carried out. Russell *et al.* (1994) considered that no extrapolation should be carried out without prior calibration, while Vanclooster *et al.* (2000) judged that calibration should be avoided wherever possible.

Targeted Parameter Estimation

Degradation and sorption parameters are environmental fate variables of particular importance in the registration of pesticides. Half-lives and sorption distribution coefficients are typically derived from controlled experiments in the laboratory, but there is continuing debate as to whether these are suitable for describing the field behaviour of compounds (Beulke *et al.*, 2000). A possible supplement to laboratory determinations is to use data measured in field or lysimeter experiments to estimate sorption and degradation parameters through calibration of a pesticide leaching model (Gottesbüren, 1998; Dubus *et al.*, 2000; Gottesbüren *et al.*, 2001). The approach consists in calibrating a pesticide leaching model against field data such as

pesticide residue profiles in soil, concentrations in drainflow or concentrations in lysimeter leachate thereby back-estimating sorption and degradation parameters. Although the calibration could be carried out using a traditional trial-and-error approach, it is often performed automatically using parameter estimation packages such as PEST (Doherty, 2000), UCODE (Poeter & Hill, 1998) or SUFI (Abbaspour *et al.*, 1997). The general approach of estimating values for input parameters through model calibration is commonly referred to as 'inverse modelling' (Poeter & Hill, 1997).

ISSUES ASSOCIATED WITH THE CALIBRATION OF PESTICIDE LEACHING MODELS

Data Requirements

Most of the data used for calibration in registration modelling are collected in field and lysimeter experiments. The amount of information collected in the field depends on the purpose of the study and differs significantly between field experiments carried out for research and those performed for regulatory purposes. Information should not be collected in the field only because it has been collected in the past (Loague, 1992) and Diekkrüger *et al.* (1995) suggested that more effort is put into the improvement of field measurement techniques rather than in the development of new models. Data which are useful for a modeller when simulating the results of a field study are site-specific meteorological data (including those necessary to calculate potential evapotranspiration using the Penman-Monteith equation: air temperatures, wind speed, humidity, sunshine hours or solar radiation); a detailed soil profile description, including soil structure; basic soil properties (such as organic carbon content, particle size distribution, soil pH where the fate of ionisable compounds is simulated, bulk density); water retention properties of the soil; an assessment of soil variability at the field scale; the actual application rate of the compound and the proportion reaching the soil; an estimation of crop development; sorption and degradation parameters specific to the experimental soil (ideally at

different depths); complete mass balances of water and solutes including a non-reactive tracer (where possible); residue profiles; and, measurements of fluxes. Although these determinations represent additional costs, their absence would contribute to uncertainty in the modelling. Bromide is often used in field experiments carried out for research purposes as an inert (*i.e.* non-degraded, non-sorbed) tracer and may provide information on soil hydrology and the extent of solute dispersion (Jones & Russell, 2000). However, concerns about the suitability of bromide profiles to assess the transport components in models have recently been reiterated (Vanclooster & Boesten, 2000).

Water and solute fluxes may be highly dynamic and change rapidly with time. Flux measurements (*e.g.* concentrations in drainflow or percolation) should thus be made at an adequate temporal resolution. A fine resolution is particularly required when preferential flow processes are an important pathway of transport or when volatilisation is to be estimated from the measurement of pesticide concentrations close to the surface in the hours and days following application (Jarvis, 1999).

The nature, quantity and quality of data have a particular importance in calibration (Yapo *et al.*, 1996) as this will partly determine whether the calibration problem is 'ill-posed' or 'well-posed' (Carrera & Neuman, 1986). Inverse modelling has been widely used in soil water physics to estimate soil hydraulic properties, such as the parameters of the van Genuchten-Mualem model (Mualem, 1976; van Genuchten, 1980), from transient outflow experiments. If water outflow data are used on their own, the calibration problem is ill-posed and non-uniqueness issues are encountered. The inclusion of additional data such as water content or water tension will stabilise the inverse problem and allow a robust estimation of hydraulic parameters, provided the data are of quality (Hopmans & Šimunek, 1999). The identification of the data requirements for an effective and robust calibration of pesticide leaching models (a 'well-posed' inverse problem) should be considered a research priority. Aspects of data quality are further discussed below.

Selection of a Model for Performing the Calibration

The selection of a leaching model which is potentially capable of simulating the experimental data is essential if a calibration is to be carried out (Larocque & Banton, 1996). Although detailed information on individual models is usually widely available, little guidance is available to support model selection on the basis of objective criteria. Guidance such as that generated by Pennell and coauthors (1990) would be useful. These authors provided guidelines on the selection of a specific leaching model (CMLS, PRZM, LEACHP, MOUSE or GLEAMS) on the basis of the simulation of an experimental dataset using these five models. Del Re & Trevisan (1995) identified a number of criteria for selecting models, but these were generic and cannot be used to select a specific model. The lack of guidance on model selection means that the choice of a model for parameterisation and calibration usually falls to the modeller undertaking the work. Differences between models used for pesticide registration in Europe have lessened in the last few years (Travis, 2000), but they still present their specificities and it is expected that this will lead to differences in predictions. The use of an inappropriate model will lead to a poor simulation of the data (Klein, 1994; Mills & Simmons, 1998) and to the derivation of unrealistic values for input parameters where a calibration is carried out (Francaviglia *et al.*, 2000). The role of model accuracy in limiting the end use of calibrated parameters should not be overlooked.

The choice of a model may be based on a number of decision criteria including the objectives of the modelling and the availability of the data necessary to parameterise the model. For purposes of screening or general management guidance, the use of simpler models which are less data intensive is justified (Di & Aylmore, 1997). For calibration purposes within the EU registration process, it is proposed that the main criterion for the choice of a specific model is the knowledge of the main processes affecting the fate of pesticides in the field context. A set of decision rules to choose one model from the four which are mainly used for pesticide registration in Europe is proposed in Table 2-1. A detailed description of the capabilities of the different models can be found elsewhere (FOCUS, 2000). The decision criteria presented in

Table 2-1 may not lead to the selection of a single model and in these instances, a decision should be made as to what the most significant processes affecting the fate of crop protection products are. Preferential flow and pesticide volatilisation are both processes likely to dominate model selection where they have a significant impact on pesticide fate. A model which accounts for all processes affecting the fate of pesticides in the field is currently not available. The modeller therefore has to make concessions and select the least imperfect of the models available. The rationale supporting the choice of a particular model should be carefully documented.

Critical Assessment of the Experimental Data

A primary requirement for a successful calibration is that the experimental data which are used to calibrate against are of good quality. If this is not the case, then calibration should not be considered in the first place. The adequacy of the experimental data to be used for calibration should not be taken for granted since sources of error and uncertainties in experiments investigating the fate of pesticides are potentially numerous (Dubus *et al.*, 2001). Typical sources of uncertainty may include: the intrinsic variability in the field; the performance and adequacy of the sampling and measuring equipment; and, the uncertainty associated with analytical determinations (limits of detection, definitive identification of analytes). Hence, although experimental data are traditionally considered to be certain, they can be largely uncertain and variable in reality (Klein, 1994) and should be considered as such in the calibration (Jones & Russell, 2000; Francaviglia *et al.*, 2000). Although critical assessments of the experimental data have only rarely been reported in the literature, such an assessment should be considered as a prerequisite to calibration and adequately reported. Particular attention should be paid to aspects of uncertainty, the quality of replication (where appropriate) and the presence of outliers in the dataset. Attempts to understand the reasons for large variability in replicated data should be made and measures taken to address the variability in the data should be reported. Pennell *et al.* (1990) observed that the variability in

replicated bromide and pesticide concentrations was large and subsequently used the least variable depth to solute centre of mass to undertake model calibration. Within the scope of model evaluation, calibration carried out with a poor quality experimental dataset could lead to the rejection of a good model or to the acceptance of a poor one (Addiscott *et al.*, 1995). In a context of parameter estimation and extrapolation, this could result in the derivation of parameter values with limited physical meaning and specific to the situation considered.

Choice of Input Parameters to be Varied During the Calibration

The rationale behind the selection of specific model input parameters to be varied during a calibration is rarely reported in the literature. Input parameters that need to be varied in the calibration are those that are both uncertain and have a strong influence on model output. The selection of parameters should therefore be based upon a combination of information on model sensitivity and parameter uncertainty.

The degree of influence of input parameters on model predictions can be assessed through a sensitivity analysis. Sensitivity analyses vary in complexity and include one-at-a-time sensitivity analyses, analyses based on random sampling, response surface methodology and Fourier amplitude sensitivity tests (Helton, 1993). In the simplest and most common of these methods (one-at-a-time approach), each selected input parameter is varied and the impact of this variation on model output is scrutinised. Recently, sensitivity analyses have been carried out for the four leaching models used for pesticide registration in Europe using four different scenarios and one-at-a-time and Monte Carlo approaches (Dubus *et al.*, 2000; Dubus & Brown, 2002). Information on the sensitivity of these leaching models has also been reported by Fontaine *et al.* (1992), Jarvis (1991), Smith *et al.* (1991), Boesten (1991), and Boesten and van der Linden (1991). Results of sensitivity analyses tend to depend on the initial scenario considered (Ferreira *et al.*, 1995) and the sensitivity of the model also varies with the output considered (*e.g.* pesticide losses by leaching, drainflow or run-off). Consequently, although these studies give a general idea about

the most influential parameters for a particular model and for particular scenarios, it is recommended that a limited sensitivity analysis is carried out if environmental conditions or pesticide properties in the modelling differ from those for which sensitivity information is available.

Some modellers consider that calibration should be restricted to those parameters which are non-measurable and parameters for which site-specific measurements are not available (Bergström, 1996). It is the opinion of the authors that parameters for which site-specific estimations are available should nevertheless be allowed to vary in the calibration albeit to a limited extent because their values are still uncertain (due to spatial variability and uncertainty arising from the laboratory and analytical procedures) and because they may not be representative of field behaviour (Beulke *et al.*, 2000). An example of such a procedure was presented by Klein *et al.* (2000). Although field capacity was measured independently, it was allowed to vary in their calibration on the basis that field capacity had only operational significance. Parameter values determined from empirical relationships such as pedotransfer functions (*e.g.* for the determination of the water retention curve or the hydraulic conductivity at saturation) should be considered uncertain and may need to be included in the calibration if it is found that they have a significant influence on model predictions. Potential evapotranspiration (PET) data can be determined using a variety of equations which will lead to different estimates and should therefore be considered to be uncertain. PET data are expected to have a major impact on calculated water balances (Dubus & Brown, 2002).

There is general consensus on the need to use sensitivity and uncertainty information for selecting those parameters to be included in a calibration, but further research is required to identify the optimum number of parameters to be varied to allow a robust calibration of pesticide leaching models.

Trial-and-Error *vs.* Automated Calibration

Calibration of pesticide leaching models is traditionally performed in a non-automated way (“manual” or "trial-and-error" calibration). This consists in manually modifying values for a small number of input parameters selected by the model user, running the model and examining the output files to see whether the modification led to a better description of the experimental data. This iterative procedure is repeated until the modeller is satisfied with the improvement in the fit between model predictions and experimental data. Manual calibration offers advantages where data are sparse and of poor quality and where expert judgement is required to assess the reasonableness of parameter estimates. However, manual calibration also suffers from a number of shortcomings including the subjectivity in a visual assessment of the fit between measured and predicted data (Loague & Green, 1991), the subjectivity in making the decision to end the calibration (Dubus *et al.*, 2000), the difficulty in dealing with the calibration of more than two parameters at a time (Janssen & Heuberger, 1995), the lack of statistical information on the calibrated parameters (Poeter & Hill, 1997), the lack of explicit assessment of the confidence that should be assigned to the calibration (Madsen, 2000) and the tedious and time-consuming aspects of this process (Yapo *et al.*, 1998; Vanclooster *et al.*, 2000). Furthermore, when a mismatch between data and model is obtained, it is difficult to know if this originates from model deficiencies or from an incomplete adjustment of the parameters (Janssen & Heuberger, 1995).

Software packages enabling the automation of the calibration process for complex models have been developed in the early 1990s and are now widely used, especially in the fields of groundwater flow modelling (Yeh, 1986; Poeter & Hill, 1997) and soil water physics (Hopmans & Šimunek, 1999). The principle consists in the minimisation of an objective function (usually the weighted sum of squared residuals between measured data and model predictions) through the modification of selected input parameters in an iterative process. Modification of the model input is based on a variety of non-linear estimation algorithms, such as the steepest descent, Gauss-Newton, Gauss-Marquardt-Levenberg and simplex procedures, which aim at keeping

the number of iterations to a minimum. Prior information on the parameters including limits to their variation can be integrated into the calibration. Stand-alone packages such as PEST (Doherty, 2000) or UCODE (Poeter & Hill, 1998) can be linked to virtually any DOS model (including the leaching models used for pesticide registration in Europe) without the need for modification of the model code. The packages will take control of the entire calibration process by running the model, examining the discrepancy between model output and experimental data, and adjusting selected input parameters. These steps are repeated until an optimised fit between model predictions and experimental data is achieved and statistical information on the quality of the calibration is generated. Examples of the application of automated calibration procedures to pesticide leaching models have been reported (Gottesbüren, 1998; Dubus *et al.*, 2000; Gottesbüren *et al.*, 2001). Guidelines for calibrating models using automated techniques have been provided by Hill (1998).

The choice of a particular mode of calibration (manual *vs.* automatic) should be left to the modeller, but it should be thoroughly justified. It is the opinion of the authors that pesticide fate modellers should be encouraged to use automatic techniques for calibration, as this can help to establish the confidence to be assigned to calibrated values. It is essential, however, that the modeller remains active in the calibration through critical evaluation of all stages of the process.

Difficulties in the Comparison of Model Output and Experimental Data

Investigations of the fate of a crop protection product in the field can involve a wide range of measurements. Data which are traditionally used in model calibration within regulatory modelling are: i) pesticide residues in soil for different times and depths (field leaching and dissipation studies); ii) concentration of pesticides at a given depth in water extracted by suction samplers (field leaching study); iii) drainflow and concentration of pesticides in drainflow (field drainflow study); and iv) water flow at the bottom of lysimeters, concentrations of pesticides in the

leachate, total loss by leaching and final soil residue profile (lysimeter study). Additional data may comprise the distribution of soil moisture within the profile, measurements of water tension and height of any water table. Ideally, the observations should comprise fluxes (*i.e.* water flows and pesticide concentrations) as well as mass balances for water and solutes. Flux measurements enable the identification of preferential flow phenomena and the comparison of model output to patterns, peak magnitude, values at each individual sampling point or values integrated over a time period. Flux measurements for water permit an independent assessment of the hydrological component of a model (Jarvis *et al.*, 1995).

A direct comparison between the measured data and outputs from leaching models is rarely possible and in most instances, model predictions will need post-processing before the model can be calibrated. A number of solutions to the difficulties encountered when comparing model output and pesticide residues, suction sampler, lysimeter or drainflow data are proposed below.

Pesticide residues in the soil profile

Pesticide residue data consist of the amount of the compound at different depths in the profile. The parameterisation of the profile in a modelling exercise requires the definition of layers, but those may differ from the layers used in the field sampling (pesticide residues are typically sampled in 5 to 10 cm increments in the topsoil). Where a match between modelling and sampling depth cannot be obtained, weighted averages of model outputs for each modelling layer will be required to enable a comparison between model predictions and experimental values.

Suction samplers

Although suction samplers are widely used to assess the leaching potential of pesticides in the field, they provide a challenge to the modeller who wishes to simulate the field data collected. Suction samplers extract water from a soil volume which is related to the suction applied and the characteristics of the soil (Litaor, 1988). In contrast, pesticide leaching models produce an output value for a layer comprised between two different depths (the value reported is usually the average for

the layer) and a direct comparison between suction sampler data and model output is thus not valid. Spatial averaging of the model output across different layers is necessary, but there is a difficulty related to its extent since the radius of the soil volume of extraction may lie between 0.1 and 0.5 m (Grosmann & Udluft, 1991).

Lysimeters

Lysimeters are hydrologically isolated soil cores instrumented to allow the collection of the water flowing at their base. Samples of leachate are collected on discrete dates often with irregular time intervals between sampling points. Any pesticide concentrations measured are an integration over time with the integration time varying from one sample to the next. Most pesticide leaching models produce output on a regular time-step (hour, day, month or year) and are not designed to output integrated concentrations over time. A direct comparison between concentrations measured in lysimeter leachate and the model output for the sampling date is thus an inadequate procedure. Model output for flow and pesticide leaching must be integrated over time between the last and the actual sampling date by accumulation and calculation of a flow-weighted average pesticide concentration, respectively (Shirmohammadi & Knisel, 1994).

Field drainflow studies

Field drainflow studies monitor the flow of water and concentrations of pesticides at the outlet of a field drainage system. Water flow is usually monitored continuously using an automatic flow meter whereas water samples are generally collected at irregular intervals for pesticide determination and quantification. Since a pesticide leaching model produces output with a regular time-step, the comparison with total loadings estimated in the drainflow study is difficult. The modeller needs to make assumptions on the pattern of pesticide concentrations between sampling occasions. The modeller may assume stable concentrations between the two sampling times (at the concentration for the first sample) or a linear interpolation of concentrations between successive samples (Kumar & Kanwar, 1997).

Visual *vs.* Numerical Assessment of Fit

The calibration of models against experimental data is based on an iterative procedure where input parameters are varied at each iteration. Reasons for stopping the calibration may include the achievement of a fit between measured and simulated data which is considered "acceptable" or the inability to improve the fit any further. The goodness-of-fit (or lack-of-fit) of the model predictions to the measured data may be assessed graphically or by using a range of indices. Graphical displays are typically used when a trial-and-error calibration is carried out. These most often plot i) changes in a variable as a function of time or depth; and, ii) the measured data against the simulated data. Although they are useful for showing trends, types of error and distribution patterns (Loague & Green, 1991), the level of adequacy between simulated and measured data to be considered "acceptable" is user-dependent and this limits the use of such displays. Also, graphical displays may not be adequate for examining the discrepancy between model and simulated data or for revealing problems with models as demonstrated by Kirchner *et al.* (1996) using two simple linear models.

A number of numerical indices have been used to try to reduce the subjectivity introduced by the modeller into the evaluation of model performance. These include the total error (TE), the maximum error (ME), the root mean square error (RMSE), the scaled root mean square error (SRMSE), the coefficient of determination (CD), the model efficiency (ME or EF), the Nash-Sutcliffe coefficient (CNS), the average difference (AVDIF), the coefficient of shape (CS), the cumulative value test (CVT), the coefficient of residual mass (CRM), linear regressions and the t- and F-tests. The reader is referred to Loague and Green (1991) and Janssen and Heuberger (1995) for detailed mathematical expressions of these indices. The automatic calibration of models using dedicated packages usually relies on the minimisation of an objective function defined as the weighted sum of squared residuals between observed and measured data. Although statistical indices have been increasingly used in the comparison between measured and simulated data, standards and even the usefulness of these goodness-of-fit indices have not yet been established for the various

applications in which they might be used (Loague, 1992). Several of these statistics are sensitive to a few large errors, especially in small datasets (Loague & Green, 1991). Also, goodness-of-fit statistics do not take into account temporal offsets of the model predictions against experimental data. A timing difference in the prediction of onset of drainflow of a few hours over a period such as a whole winter is of little consequence for the interpretation of results, but may have a major effect on goodness-of-fit statistics (Armstrong *et al.*, 1996). Furthermore, the choice of levels of fit deemed acceptable defaults to the modeller and the goodness-of-fit is therefore subjective. Typical tests are probably not sufficiently strict to convince model skeptics about the accuracy and usefulness of models and there would be a need for the establishment of agreed performance criteria (Jarvis, 1999) that invalid models are unlikely to pass (Kirchner *et al.*, 1996). Both graphical and numerical methods have limitations when considered individually (Loague & Green, 1991) and the combination of the two sets of techniques should be preferred (Gaunt *et al.*, 1997; Borah & Kalita, 1999).

Sequential Procedures in Calibration

The general consensus is that the most appropriate procedure for calibrating models is first to calibrate the hydrology of the model to provide a reasonable representation of water movement at the experimental site and then to calibrate the solute transport component of the model (Armstrong *et al.*, 1996; Jones & Russell, 2000; Durborow *et al.*, 2000). It is generally considered that parameters calibrated against soil hydrology should be left unchanged during the calibration against pesticide data (Borah & Kalita, 1999). Although these general procedures are desirable, it may not always be possible to get a good fit to the hydrology or to derive a unique set of calibrated values. Whilst some authors claim that having a good simulation of water fluxes is necessary to predict both pesticide fluxes and concentrations accurately, simulating a good fit to the pesticide data with an inadequate description of the hydrology is possible (Gottesbüren *et al.*, 2000). Data for a non-interactive tracer such as bromide are frequently used as an intermediate step between calibration of

hydraulic and pesticide routines. However, in a number of evaluation exercises where bromide was used, a simultaneous good model fit to the water, bromide and pesticide data was not possible (Thorsen *et al.*, 1998; Jarvis *et al.*, 2000). Given these limitations and the uncertainty associated with both the model input parameters and the hydrological data, the modification of parameter values which were calibrated against the hydrology during a calibration of the pesticide section of the model can be justified provided that the hydrology-calibrated parameters are only varied within the bounds of their uncertainty and that the fit to the hydrology still meets the acceptability criteria of the modeller. Such conditional calibrations can be automated using packages such as PEST when used in its regularisation mode (Doherty, 2000). In specific instances (*e.g.* parameter estimation), a simultaneous calibration of the water and pesticide components of leaching models may be more appropriate as a sequential calibration might lead to the derivation of lumped parameters. Parameter lumping is treated in more detail in the next section.

Potential Pitfalls in the Calibration of Pesticide Leaching Models

Pesticide leaching models are large, non-linear, complex simulation systems and may hence suffer from non-uniqueness with regard to the set of calibrated parameters (Spear, 1997). Non-uniqueness occurs when different combinations of parameters or parameter values provide an equally good fit to the data and commonly results from large correlation between input parameters in the model and/or when the data are insufficient in terms of quantity and quality with respect to the number of parameters to be identified through model calibration. Pesticide fate models are likely to be subject to non-uniqueness issues because of their non-linear character and the inherent compensation of a number of parameters with regard to the prediction of pesticide loss (*e.g.* sorption and degradation parameters with respect to total leaching). Non-uniqueness issues in the calibration of pesticide leaching models remain largely unnoticed when a manual calibration is carried out and are best revealed using automated calibration techniques (Poeter & Hill, 1997). Calibration uniqueness when deriving sorption and degradation parameters may be assessed by

using different sets of starting values (Isabel & Villeneuve, 1986; Madsen, 2000) or response surface analysis (Toorman *et al.*, 1992; Šimunek *et al.*, 1998). Additional research should be carried out to estimate the extent of non-uniqueness in the calibration of pesticide leaching models. The use of methodologies incorporating a framework for dealing with non-uniqueness in parameter estimation and subsequent extrapolation, such as that proposed by Beven and Binley (1992), deserve investigation.

Another pitfall of calibration is the 'lumping' of parameters. Here, lumping refers to the attribution to a parameter of a value that does not reflect its theoretical meaning. This is held to occur during the calibration process, rather than being inherent in the model. Lumping may originate from the facts that i) the model may not be intrinsically capable of simulating the experimental data (*e.g.* by not including a description of key processes affecting the fate of pesticides), ii) the data may be of poor quality and uncertain, iii) other model input parameters may have been attributed inadequate values, or iv) multiple sets of parameter values may satisfy the conditions to be a solution in ill-posed calibration problems. Lumping thus reflects inaccuracies, uncertainties and limitations associated with experimental data, modelling and calibration. Lumped parameters can usually only be obtained by calibration and have lost their physical, chemical or biological definition. Hence, lumped values will only be valid for the specific set of conditions for which they were obtained and will be of little value for deriving information regarding the specific processes controlling transport and fate (Brusseau, 1998) and for extrapolation purposes.

The degree of influence of the modeller on calibration results is also a significant issue in calibration. Since calibration procedures are left to the discretion of the modeller, differences are expected with respect to the selection of parameters to be calibrated, the variation applied to their values, the setting up of automatic calibration packages, where appropriate, and the assessment of the goodness-of-fit between measured and simulated data. The user-subjectivity in the parameterisation

and calibration of pesticide leaching models is established (Brown *et al.*, 1996; Boesten, 2000) and may prevent model evaluation in some instances (Tiktak, 2000).

There are numerous examples of calibrated values substantially differing from the values initially expected for the scenario considered (*i.e.* those used in the initial parameterisation of the model). Carsel *et al.* (1985) calibrated the PRZM model against field data for leaching of aldicarb and both the decay constant in the lower zone and the linear sorption distribution coefficient had to be increased by a factor of ca. two to reach an adequate description of the data. Francaviglia *et al.* (2000) reported the need for the use of unrealistic values of bulk density and field capacity to calibrate PELMO against a lysimeter dataset. Mills and Simmons (1998) had to increase laboratory sorption values in the top 5 cm of the soil by a factor of 10 and consider a linear increase of dispersion with depth to improve their fit to the data. Similarly, sorption coefficients for aldicarb derived from a calibration were outside the literature range (Lorber & Offutt, 1986). Villholth *et al.* (2000) found that the sorption distribution coefficient derived by calibration against experimental data were about an order of magnitude smaller than that derived in the laboratory. Thorsen *et al.* (1998) could only improve the simulation of the leaching of a pesticide in lysimeters by violating the physical description of the soil column.

Assessment of the Parameter Values Derived from Calibration

Owing to the non-uniqueness of calibrations and the potential for parameter lumping, changes in parameter values resulting from calibration need to be carefully assessed. Two approaches are typically used. First, calibrated parameters can be assessed against values used in the initial input file. Initial values usually reflect the best estimate of an adequate value the modeller can make on the basis of laboratory or field experiments, review of the literature or expert judgement. It is particularly critical to assess whether a calibrated value falls within the range of uncertainty expected for a particular parameter. Although calibrated pesticide properties derived by Carsel *et al.* (1985) were varied within a factor of ca. two of the initial estimates

for these parameters, they were within the range of uncertainty as estimated by a literature review.

The second approach to assess parameter values derived by model calibration is to use the calibrated values to generate model output which can then be compared to data different from that used in the calibration. Thorsen *et al.* (1998) consider that parameter values derived against an experiment under controlled conditions where less complex environmental conditions prevail should be tested against a dataset acquired under more complex conditions. The cross-validation step of the calibrated parameters against a dataset different from that used in the calibration is considered important (Janssen & Heuberger, 1995), especially if the calibration is used to derive values for sorption and degradation which are to be considered within pesticide registration (Gottesbüren *et al.*, 2001). Such testing exercises may include in the case of a field drainflow study, i) the calibration of the model hydrology against soil moisture contents in the profile and a verification against drainflow volumes; ii) the calibration of the model against pesticide residues and a verification against pesticide concentrations in drainflow although the use of soil residue data for assessing pesticide leaching has been questioned (Jarvis *et al.*, 1995; Malone *et al.*, 2000); and, iii) the calibration of the model against data for one year and a verification against a subsequent year. Data collected in independent experiments have also been used for cross-validation. Gottesbüren *et al.* (2001) estimated sorption and degradation parameter values by calibrating PEARL and PESTRAS against lysimeter data and tested the optimised values against data for pesticide residues from a field experiment. However, the additional experimental data available could be directly integrated into the calibration instead of being used for separate evaluation. Increasing the amount of data available for calibration is expected to decrease the ill-posed nature of the calibration problem and hence non-uniqueness issues in the calibrated parameter sets (Hopmans & Šimunek, 1999). A possible refinement to the calibration of pesticide leaching models and the evaluation of calibrated parameter sets could therefore include, i) an initial parameter estimation based on a calibration against a given experimental dataset; ii) a simulation using calibrated parameters with a comparison to data different from those used in the initial calibration; and iii)

a model calibration integrating all available experimental data using calibrated values derived in step (i) as starting values for parameters to be estimated and strict limits on the variation of these parameters.

A discrepancy between measured and simulated data in the cross-validation run may not solely be attributed to inadequate calibrated parameter values since the lack-of-fit might also be due to model deficiencies (the cross validation is sometimes used as a model testing method) or the attribution of inadequate values to parameters other than the calibrated ones. Parameters should not be allowed to be varied outside their "reasonable range" during the calibration (Borah & Kalita, 1999; Jones & Russell, 2000) and setting a parameter to a specific value merely to achieve a good fit to the measured data should be avoided (Klein *et al.*, 2000). In some instances, substantial effort put into a calibration does not significantly improve the fit to the data. A poor match may suggest an inadequacy in the conceptual model, an error in the numerical solution, a poor set of parameter values, a poor set of experimental values or some combination of these. It may not be possible to distinguish between these different sources of error. Discrepancies between expected and calibrated values should be discussed and assumptions on the likely cause of such discrepancies proposed. The uncertainty left in the model parameters after calibration should be acknowledged and adequately accounted for in subsequent model applications (Janssen & Heuberger, 1995).

GUIDELINES FOR THE REPORTING OF CALIBRATION ACTIVITIES

Given the diversity in modelling situations and the importance of written communication when regulators assess modelling studies, it appears that the most appropriate way to improve quality in the modelling (including model parameterisation and calibration) and to decrease the associated uncertainty is to issue guidelines on the reporting of the modelling. Such guidance provides flexibility to modellers as opposed to guidelines on the modelling itself (Kirchner *et*

al., 1996). Recommendations for parameterising and calibrating pesticide leaching models have been issued and have highlighted the need for quality reporting (CAMASE, 1995; Resseler *et al.*, 1997; Jones & Russell, 2000). However, the aspects that should be included in reports have not been explicitly set out. Guidance on the reporting of calibration activities with pesticide leaching models is proposed in Table 2-2. The guidelines are intended to be non country-specific and are generic in nature. It is hoped that the guidelines will raise awareness among modellers of the issues associated with the calibration of pesticide leaching models. Their use is expected to improve calibration activities as a whole and help modellers and regulators to assess the confidence that should be attributed to predictions based on calibrated parameters.

CONCLUSIONS

Complex deterministic models are being used in pesticide registration in Europe to assess the potential for a pesticide to impact on the environment. Within this context, calibration may be used to derive input parameters which are difficult to obtain from independent measurements, to back-derive targeted parameter values, to validate the use of a model or to establish the basis for subsequent extrapolations. The need for calibration is controversial within the pesticide modelling community. Some individuals consider that calibration is a prerequisite to a reliable simulation of pesticide fate whereas others argue that a calibrated set of parameters is only valid for the conditions at hand and should not be used for other scenarios.

The calibration of leaching models is clearly one of the most arduous tasks a pesticide fate modeller is faced with. The success of a calibration is primarily limited by the nature, amount and quality of the available data, the appropriateness of the model used, the effectiveness of the applied calibration technique, the time available, computer power, expertise and financial resources (Janssen & Heuberger, 1995; Gottesbüren *et al.*, 2000). Within the scope of the calibration of pesticide leaching models, the main factors which may lead to inappropriate calibrations

include the lack of substantial data or their poor quality, the use of a model which is not capable of describing the experimental dataset, the inadequate selection of parameters to be varied and inadequate calibration procedures. Given these uncertainties, the inherent nature of pesticide leaching models (non-linearity, large correlation between parameters) and the differences between calibration approaches adopted by individuals, it is clear that interpreting the strength of a calibration and resulting model output is no simple matter. The default assumption should be that calibration results are uncertain, if not demonstrated otherwise.

Given the importance of calibration activities within pesticide registration and their potential limitations, the regulator should be provided with sufficient information to allow an assessment of the confidence to be assigned to results from calibration or from extrapolation based on calibrated parameters. Use of the guidelines proposed in the present paper would help regulators in their assessment and indirectly improve calibration practice.

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Table 2-1. Set of decision criteria to assist in the selection of a specific model for describing field data and performing calibrations. Only those leaching models selected by the FOCUS groundwater scenarios working group are considered. Brackets indicate that the use of the model is possible although the parameterisation is not straightforward.

Decision criteria	Model(s) suggested
Accounting for pesticide losses by volatilisation	PEARL, PELMO, PRZM
Evidence or strong suspicion of a significant influence of preferential flow on water hydrology or pesticide loss	MACRO
Simulation of complex degradation schemes	PELMO, PEARL
Simulation of the fate of compounds susceptible to ionisation	PEARL, PELMO, (PRZM), (MACRO)
Simulation of the interaction between the unsaturated zone and the upper groundwater	PEARL
Need for an accurate description of soil hydrology	MACRO, PEARL
Simulation of lysimeter experiments	PEARL, MACRO, PELMO[a], PRZM[a]
Increase in sorption with time	PEARL, PRZM, PELMO, (MACRO)

[a] PELMO does not integrate a bottom boundary condition specific to the simulation of lysimeter flow, but the model has been considered capable of describing lysimeter datasets for coarse-textured soils (Klein *et al.*, 1997). Given the similarities between PELMO and PRZM, it is anticipated that this conclusion can be extended to PRZM.

Table 2-2. Guidelines on the reporting of calibration activities carried out for pesticide registration. Reporting of calibration activities are expected to provide answers to the following questions.

Introduction
What was (were) the specific aim(s) of the calibration?
Has there been any previous modelling activity for either the experimental site or the compound of interest?
Critical assessment of the experimental data used for calibration
What data were measured in the experimental study?
How many replicates were there?
What was the quality of the replication?
Were any unusual conditions experienced during the experimental period (weather conditions; flooding or freezing conditions)?
Were there difficulties with regard to operational (*e.g.* failure of the monitoring equipment) or analytical procedures (*e.g.* analytical replication)?
What were the limits of detection and quantification?
Were difficulties encountered in the identification or quantification of compounds?
Were there missing data for a period? Were there outliers?
What were the main uncertainties related to the data? What overall confidence should be assigned to the experimental data?
Detailed justification of the choice of a specific pesticide leaching model for the calibration
Which model (version, release date) was used?
What was the rationale behind the choice of the particular model used?
Is the model a priori suitable for describing the experimental data?

Were there processes important for describing the data not explicitly accounted for in the model? if so, were these processes accounted for in the modelling?

Have there been previous studies conducted with this model with the same compound? With the same soil? How did the model perform?

Detailed description of the initial parameterisation of the model and of the selection of parameters to be calibrated

How were values for the input parameters chosen for the initial parameterisation? Which values were determined by independent experiments? Which were determined by expert judgement or educated guess?

Where did the main uncertainties in the parameterisation lie?

Was information on the sensitivity of the model available? Was the sensitivity information transferable to the current modelling exercise?

If either no information was available on the sensitivity of the model or the information was not transferable, was a small scale sensitivity analysis conducted?

If a small scale sensitivity analysis was not conducted, how were the parameters to be varied in the calibration selected?

Detailed description of the calibration procedures used

Which experimental data were used in the calibration?

In the case where replicates were available, were the data for only one replicate considered in the calibration? Alternatively, how was the information from the different replicates combined? How was conflicting replication handled (*e.g.* differences in flow volumes for a replicated lysimeter experiment)?

How were concentrations below the limit of quantification handled?

How were outliers or missing samples (where applicable) handled?

What were the assumptions made for the concentrations between two sampling dates (drainflow studies)?

Which model output(s) was used in the calibration?

Could the model output be directly compared to the experiment data (note that a post-processing is required in most cases)? If not, how was model output or the experimental data post-processed? Provide a numerical description of the post-processing performed.

Was the calibration done manually (trial-and-error calibration) or was it performed automatically?

In the case of a manual calibration

How was the goodness-of-fit between model output and experimental data assessed? Visually through graphical displays? Numerically using statistical indices? Using both types of assessment?

What was the main target of the calibration? Was it peak values, low values, average values, timing of peaks, first detection, detailed pattern, general trend?

Was the calibration performed sequentially (*e.g.* calibration of the hydrological part of the model then calibration of the pesticide section)?

Were parameters calibrated sequentially for one particular set of output (*i.e.* one parameter after the other)?

How many runs were carried out to achieve the end results?

What criterion was used to stop the calibration?

In the case of an automatic calibration

Which package was used? Which version of the package?

How was the objective function defined?

Were (some) parameters transformed?

Which weights were assigned to the experimental observations?

Was any relationship specified between parameters?

Were all the input parameters calibrated simultaneously?

How many iterations and runs were necessary to achieve convergence?

Were consistent calibration results obtained when different starting values were specified?

What was the correlation between parameters during the calibration (as reported by the calibration package)?

Did the residuals show a particular pattern or were they randomly distributed?

Was the visual examination of the fit to the observations satisfactory when using the final set of calibrated parameters?

Assessment of calibration results

By how much did the parameters have to be changed to get a good fit to the data? Are the calibrated values plausible? Reasonable? Do they fit with what is known about the variability and uncertainty of these parameters?

Was a satisfactory (visually and statistically) fit to the data obtained? If not, what could it be attributed to (Inadequate choice of parameters to be varied? Inadequate values for parameters not included in the calibration? Inadequate calibration procedures? Inability of the model to describe the data?)?

Cross-validation of the set of calibrated parameters against other model output or against another field dataset

How much uncertainty has been left in the parameters after calibration?

Does the calibrated parameter set give satisfactory results when considering an output other than that used for the calibration?

Is there a good fit between model predictions and experimental data when the calibrated set of parameters is used to describe another dataset?

Conclusions

How much confidence should be assigned to the final values attributed to the parameters? Where do the uncertainties lie?

Can the results of the calibration be used for the intended purpose defined in the introduction?

Tables and figures

The following tables and figures are useful to assess the confidence that should be assigned to the calibration results:

A comparative table with initial (from the initial model parameterisation) and final (calibrated) values for the parameters included in the calibration,

A table comparing values of statistical indices (at least the sum of squared residuals) before and after the calibration (where appropriate),

A figure showing a comparison between the experimental data and the model predictions for the initial and calibrated runs (charts against time or depth for the variable used in the calibration),

A figure showing a comparison between the experimental data and the model predictions for the initial and calibrated runs (charts against time or depth for the variable(s) measured in the field, but not used in the calibration),

A figure plotting measured *vs.* simulated data with a line of perfect agreement (or 1:1 line) for the variable used in the calibration and for other variables measured in the field, but not used in the calibration.

Chapter 3

SENSITIVITY ANALYSES FOR LEACHING MODELS USED FOR PESTICIDE REGISTRATION IN EUROPE

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ABSTRACT

Sensitivity analyses using a one-at-a-time approach were carried out for leaching models 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. 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

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(Freundlich exponent and distribution coefficient) and degradation (either degradation rates or DT50, 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.

INTRODUCTION

Sensitivity analysis of mathematical models aims at ranking input parameters according to their influence on model predictions (Fontaine *et al.*, 1992). 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 (Fontaine *et al.*, 1992; Hamby, 1995) and evaluation (Hamby, 1995; Wolt, 2002) since it provides the modeller with an opportunity to identify deficiencies in the theoretical structure of models (Del Re & Trevisan, 1993) and problems in their operation (Fontaine *et al.*, 1992). Secondly, sensitivity information can be used for model simplification and refinement (Iman & Helton, 1988). 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 (Del Re & Trevisan, 1993) or eliminating those terms utilising the parameter (Fontaine *et al.*, 1992). Thirdly, it can help to identify those parameters which require the greatest accuracy in their determination (Boesten, 1991) and which require the most (or least) attention when parameterising models (Ferreira *et al.*, 1995; Dubus & Brown, 2002). Also, sensitivity information is useful to select the relative priority of parameters to be varied when model calibration is undertaken (Soutter & Musy, 1999; Dubus *et al.*, 2002) or to be included in probabilistic modelling (Labieniec *et al.*, 1997). Fourthly, sensitivity information is useful to interpret model output effectively (Iman and Helton, 1988; Wolt, 2002) and improve the credibility of modelling results

(Wauchope, 1992). Finally, the information can be used for guiding effort in data collection for deriving model input parameters (Soutter and Musy, 1998), designing field studies (Wolt, 2002), but also for identifying areas where additional research and further model development is needed (Fontaine *et al.*, 1992; Hamby, 1994).

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 are mainly used in Europe for assessing potential for leaching to groundwater within the scope of pesticide registration: PRZM (Carsel *et al.*, 1984; Carsel *et al.*, 1998), PELMO (Klein, 1991; Jene, 1998), PESTLA/PEARL (Boesten & van der Linden, 1991; van den Berg & Boesten, 1999; Tiktak *et al.*, 2000) and MACRO (Jarvis, 1991; Jarvis & Larsson, 1998). Some information on the sensitivity of these models exists (Fontaine *et al.*, 1992; Wolt, 2002; Del Re & Trevisan, 1993, Boesten, 1991; Dubus & Brown, 2002; Boesten & van der Linden, 1991; Jarvis, 1991; Jarvis *et al.*, 1991; Smith *et al.*, 1991; Jones and Russell, 2000). However, the information is difficult to use in practice because sensitivity analyses i) have been conducted using a range of techniques and results may not be directly comparable from one study to another (Fontaine *et al.*, 1992; Boesten, 1991; Dubus & Brown, 2002); ii) may have concentrated on a few input parameters only (Boesten, 1991; Jarvis, 1991; Jarvis *et al.*, 1991); and iii) may have been generated for one particular scenario only (Del Re & Trevisan, 1993; Jarvis, 1991).

In order to provide results with a wide applicability, sensitivity analyses were carried out for PELMO, PRZM, PESTLA/PEARL 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.

MODELLING METHODS

Base-Case Scenarios

Results of sensitivity analyses for environmental models are known to be site and condition specific (Ferreira *et al.*, 1995). 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 Koc value of 20 ml g^{-1} and a laboratory DT50 of 7.8 days at 20°C (broadly equivalent to a field DT50 of 20 days for northern Europe) whilst Pesticide 2 has a Koc of 100 ml g^{-1} and a laboratory DT50 of 23.3 days at 20°C (broadly equivalent to a field DT50 of 60 days for northern Europe). Although hypothetical, the properties of the two compounds fall within the range of those registered for use in the UK (Dubus & Brown, 2002).

The two soils selected for the modelling were a sandy loam of the Wick series and a clay loam of the Hodnet series. These were chosen on the basis of their texture and distribution throughout England and Wales. 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, reddish 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. Soils of the Wick series and their hydrological equivalents represent 7.3% of agricultural land in

England and Wales whilst soils with a hydrology similar to that of the Hodnet series represent 8.3% of this land area (Hollis *et al.*, 1993). Selected physico-chemical properties and water retention data for the two soils are presented in Table 3-1. Both profiles were adjusted to 1-m depth to enable a comparison of leaching to depth between the two soils and to tie in with current practices in risk assessment for pesticides in groundwater within the EU (FOCUS, 2000).

A winter wheat crop was simulated in each year and emergence, maturation and harvest dates (12 October, 24 June and 7 August, respectively) were taken from Hough (1990) as representative of cereal cultivation in the UK. 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 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. Potential evapotranspiration (PET) was calculated outside the models using the Penman-Monteith equation (FAO, 1991). 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 of the two pesticides. Having the same weather data between years meant that the comparison between modelling scenarios with different duration was still meaningful.

Modelling Strategy and Automation of Modelling Tasks

Sensitivity investigations concentrated on the four models which are 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; Klein, 1991; Jene, 1998), the Pesticide Root Zone Model (PRZM; Version 3.14β, January 2000; Carsel *et al.*, 1984; Carsel *et al.*, 1998), the PESTicide Leaching and Accumulation model (PESTLA; version 3.4, September 1999; Boesten & van der Linden, 1991; van den Berg & Boesten, 1999) and the MACRO model (version 4.1, July 1998; Jarvis, 1991; Jarvis & Larsson, 1998). 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 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. The Dutch model PESTLA was extensively used for registration purposes in the Netherlands and other countries before the introduction of PEARL in 2000 (Tiktak *et al.*, 2000). The two models are similar to some extent. 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 (FOCUS, 2000).

Models were parameterised to simulate the leaching of the two pesticides in the two soils. Run-off, erosion and volatilisation were minimised 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 blind simulations were based on measured properties as much as possible. However, due to differences between model codes in terms of mathematical representation of the different processes and due to the lack of some measured parameters, initial parameterisations involved a certain degree of subjectivity (Thorsen *et al.*, 1998). 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 corrections for moisture and temperature effects on degradation were therefore activated. Degradation at depth was related to that in the topsoil using the equation implemented in MACRO_DB (Jarvis *et al.*, 1997) 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 (Freundlich exponent 0.9). Sorption distribution coefficients

(Kd) were introduced directly into the model, except for PESTLA for which a Kom (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 period before pesticide application occurred was limited to 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 package (Doherty, 2000). 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 interacts 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.

Approach to Sensitivity Analysis

Model sensitivity can be assessed using a range of techniques varying in their complexity and sophistication (Iman & Helton, 1988; Hamby, 1994). Differences between the techniques have been discussed (Helton, 1993) and assessed (Hamby, 1995). Here, we report on the simplest form of analysis, referred to as one-at-a-time sensitivity analysis (Hamby, 1994) or ceteris paribus approach (Helton, 1993). 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 (Dubus & Brown, 2002; Tiktak *et al.*, 1994). Disadvantages of the

one-at-a-time approach are that i) it is more computationally intensive than other methods when the analysis involves a large number of parameters (Hamby, 1995), ii) it is not suited to study the influence of large variations of input parameters on model predictions, and iii) 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 (Holden *et al.*, 1996; Ma *et al.*, 2000). 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 Kd values in the topsoil was supported by the same relative increase in Kd 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 3-1 to 3-4.

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 (Fontaine *et al.*, 1992; Smith *et al.*, 1991), parameters in the present study were varied within a range which reflected their uncertainty. Maximum variation ranges were assigned to input parameters by consensus amongst the three authors. In general, parameters which are determined experimentally were varied symmetrically (*i.e.* 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 3-1 to 3-4.

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 loss of pesticide via leaching. For PRZM, cumulative recharge was taken from the annual values for the 'leaching output' for the bottom layer of the 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}.

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:

$$Input\ variation = \frac{I - I_{BC}}{I_{BC}} * 100 \qquad (1)$$

$$Output\ variation = \frac{O - O_{BC}}{O_{BC}} * 100 \qquad (2)$$

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,

O_{BC} is the value of the output variable for the base-case scenario.

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

$$ROV = \frac{Output\ variation}{Input\ variation} \qquad (3)$$

Or,
$$ROV = \frac{O - O_{BC}}{I - I_{BC}} * \frac{I_{BC}}{O_{BC}} \qquad (4)$$

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 the input parameters by 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),

$$MAROV = Max_i \left| ROV \right| \qquad \text{i= 1 to r,} \qquad (5)$$

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.

The plotting of the output variation *vs.* the input variation provides a graphical means to assess the sensitivity of the model to input parameters. An example is provided in Figure 3-1 which presents results 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 *vs.* 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 MAROV might lead to an overestimation of sensitivity in instances where there is non-linearity in the response of the model to changes in input parameters (*e.g.* RPIN in Figure 3-1).

RESULTS

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 pesticide losses for the four models are presented in Table 3-2. Predicted pesticide breakthrough in leachate is presented in Figures 3-2, 3-3, 3-4 and 3-5 for PELMO, PRZM, PESTLA and MACRO, respectively. Figures 3-2 and 3-3 are presented on a monthly time-step while a daily time step was used in Figures 3-4 and 3-5. 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 were supplied to the model by selecting the option 'own ET data' , but it later transpired that the model was reading PET as actual evapotranspiration. 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 to 9 years for the different scenarios and maximum monthly

loadings were predicted to occur from 14 to 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 three to four 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 (*e.g.* 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.

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. However, predictions for pesticide losses by PELMO, PRZM and PESTLA were found to be broadly similar despite differences in absolute amounts leached. The preferential flow model MACRO strongly contrasted with the three chromatographic flow models, especially for the finer-textured Hodnet soil where different leaching pattern and magnitude were predicted.

Sensitivity of PELMO

Parameters which were found to influence prediction of percolation by PELMO are presented in Table 3-3. Results from sensitivity analyses with regard to the prediction of percolation by PELMO were mainly 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 (*i.e.* 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. Small differences in sensitivity for the two pesticides for a given soil are due to the running of PELMO for different duration for the scenarios and the prediction of a different percolation for the first year of simulation when compared to subsequent years.

In contrast to recharge, the prediction of pesticide losses was very sensitive to some parameters (MAROV>10; Figure 3-6). 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. However, whilst absolute MAROV values for this specific scenario can 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 3-6 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.

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 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 (Figure 3-7). 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 3-7 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.

Sensitivity of PESTLA

Results from the sensitivity analysis for the prediction of percolation by PESTLA are presented in Table 3-3. 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).

PESTLA predictions for pesticide losses were greatly affected by changes in input parameters (Figure 3-8). 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 Kom 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 partitioning of pesticide between the solid and liquid phase.

Sensitivity of MACRO

The sensitivity of MACRO predictions for percolation to changes in input parameters is presented in Table 3-3. No notable difference was found in the ranking of parameters between the four scenarios. The parameter 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 Figure 3-9. Maximum MAROV values for pesticide losses ranged from 3.1 (Pesticide 1 on Hodnet soil) to 22.2 (Pesticide 2 on Wick soil). The ranking of the most influential parameters was found to be influenced by both the soil and pesticide type and large differences were found. For example, ZN, the pore size distribution index was found to be the second most influential parameter in the Pesticide 2 - Hodnet combination whereas it was ranked 24th in the scenario involving Pesticide 1 and the Wick soil. 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). The importance of these parameters was particularly strong for Pesticide 2 where the parameters had MAROV values above 10. 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, tortuosity factor for the macropores) is particularly uncertain because it is difficult to determine experimentally and little guidance is available. The presence of the diffusion coefficient in water (DIFF) in the top 10 parameters is also specific to this scenario. Although the sorption coefficient (ZKD in Figure 3-9) 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). The sensitivity of the preferential flow model MACRO has been discussed in more detail elsewhere (Dubus & Brown, 2002).

DISCUSSION

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 to some extent. 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 (*e.g.* different model output considered, different main dissipation processes), it is suggested that a limited sensitivity analysis is carried out to identify those parameters which matter most in the modelling.

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 Kd values were directly fed into input files. Organic carbon content has a direct influence on the calculation of Kd values when these latter values are calculated from

partition coefficients normalised to organic carbon (Koc) or organic matter (Kom). It is therefore expected that the organic carbon content will have a significant influence on model predictions for pesticide leaching (Soutter & Musy, 1998). 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 (Flori *et al.*, 1993).

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 (Krajewski *et al.*, 1998). 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 (Boesten, 1991; Boesten & van der Linden, 1991; Persicani, 1996; Soutter & Musy, 1998). Sorption (Freundlich distribution coefficient and exponent) and degradation (DT50) parameters are traditionally determined in the laboratory and the applicability of these values to simulate field behaviour is subject to much debate (Beulke *et al.*, 2000). The field environment being inherently variable in space and time, half-lives and sorption coefficients should be considered as variable and uncertain (Wood *et al.*, 1987; Walker *et al.*, 2001). 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 (Dubus *et al.*, 2001). 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 (Tiktak *et al.*, 1994). Its influence on predictions for pesticide loss tends to increase with the strength of sorption (Boesten, 1991). Registration procedures for pesticides in the US and in Europe tend 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 is frequently overlooked. The practical implications of current practice such as averaging parameters of the non-linear Freundlich equation for different soils (Beulke *et al.*, 2001) should be investigated and the Freundlich exponent should be considered as important as Koc (or Kom) when estimating pesticide leaching at low levels (Boesten, 1991).

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 (Smith *et al.*, 1991), but can be expected since water fluxes remain a governing process for the leaching of solutes to groundwater (Soutter & Musy, 1999). 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 (Smith *et al.*, 1991) 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 US and Germany whilst other values are used elsewhere (*e.g.* –5 kPa in the UK, –10 kPa in the Netherlands). Given that no guidance is provided on which reference tension to use for defining field capacity

values in the models, these national differences are likely to introduce additional uncertainty in field capacity values and hence in model predictions.

A common preconception is that Richards' equation models, and in particular MACRO (Brown *et al.*, 2000), are more difficult to parameterise than capacity models and therefore carry a larger uncertainty in model predictions. In the present study, the number of parameters showing a large influence on predictions for pesticide loss for PESTLA and MACRO was large compared to the two capacity models PELMO and PRZM, but the magnitude of sensitivity for the two latter models exceeded that of the two models with a more complex description of hydrology for all four scenarios. This suggests that the increased uncertainty associated with the difficulty in parameterising Richards' equation models may be counterbalanced by the lesser model sensitivity when compared to capacity models and that both types of models may show similar levels of overall predictive uncertainty.

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 used to predict pesticide leaching in Europe.

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Table 3-1. 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

Table 3-2. 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	1.11×10^{-7}
Total pesticide loss predicted at 1-m depth (% of applied)	1.29	0.01	0.02	5.53×10^{-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	4.04×10^{-3}
Total pesticide loss predicted at 1-m depth (% of applied)	1.59	0.03	0.04	2.02×10^{-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	2.10×10^{-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

Table 3-3. 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 3-1 to 3-4.

Ranking	Scenario							
	Wick soil				Hodnet soil			
	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.

Appendix 3-1. PELMO input parameters considered in the sensitivity analysis and variation ranges applied.

Parameter	Description	Wick soil			Hodnet soil		
		Nominal value	Minimum value	Maximum value	Nominal value	Minimum value	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 3-2. PRZM input parameters considered in the sensitivity analysis and variation ranges applied.

Parameter	Description	Wick soil			Hodnet soil		
		Nominal value	Minimum value	Maximum value	Nominal value	Minimum value	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
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
KF [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 3-3. PESTLA input parameters considered in the sensitivity analysis and variation ranges applied.

Parameter	Description	Wick soil			Hodnet soil		
		Nominal value	Minimum value	Maximum value	Nominal value	Minimum value	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 $d^{-1/2}$) 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})	55000	41250	68750	55000	41250	68750
ENSL	Molar enthalpy of the dissolution process (J mol^{-1})	40000	20000	80000	40000	20000	80000
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 d^{-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

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 d^{-1})	0.50	0.25	0.75	0.50	0.25	0.75
SUWA	Coefficient of diffusion in water (m^2 d^{-1})	3.97×10^{-5}	8.61×10^{-6}	8.63×10^{-5}	3.97×10^{-5}	8.61×10^{-6}	8.63×10^{-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 (d)	7.76	3.88	15.52	7.76	3.88	15.52
KOM	Kom (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 (d)	23.3	11.6	46.5	23.3	11.6	46.5
KOM	Kom (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 3-4. MACRO input parameters considered in the sensitivity analysis and variation ranges applied.

Parameter	Description	Wick soil			Hodnet soil		
		Nominal value	Minimum value	Maximum value	Nominal value	Minimum value	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
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 (d^{-1})	0.0893	0.0446	0.1786	0.0893	0.0446	0.1786
DEG [a]	Degradation rates (d^{-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 (d^{-1})	0.0298	0.0149	0.0596	0.0298	0.0149	0.0596

DEG [a]	Degradation rates (d^{-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.

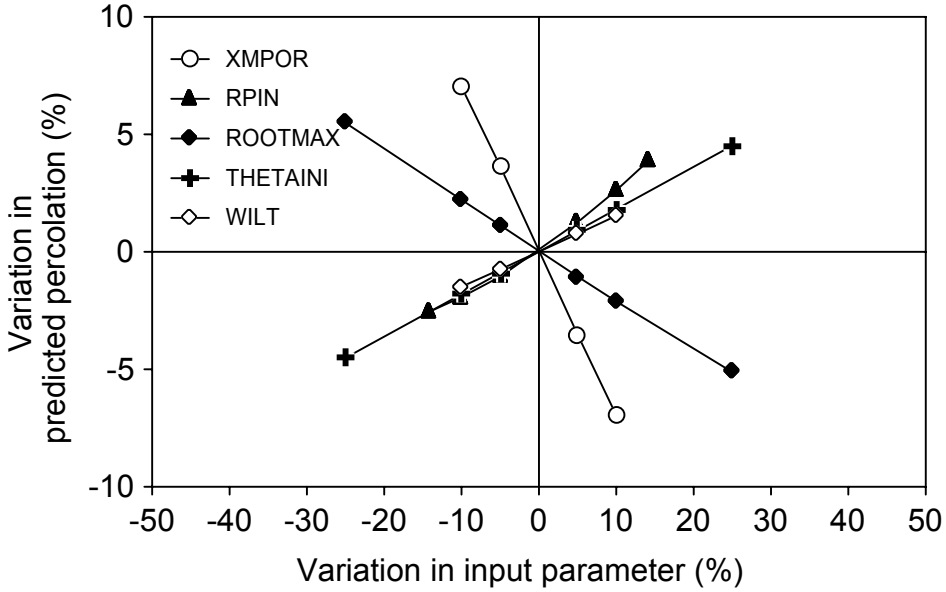

Figure 3-1. Example of chart showing the variation in MACRO predictions for percolation in response to the modification of input parameters.
Only the five parameters which have the most influence on percolation predictions are presented. A brief description of the parameters can be found in Appendix 3-4.

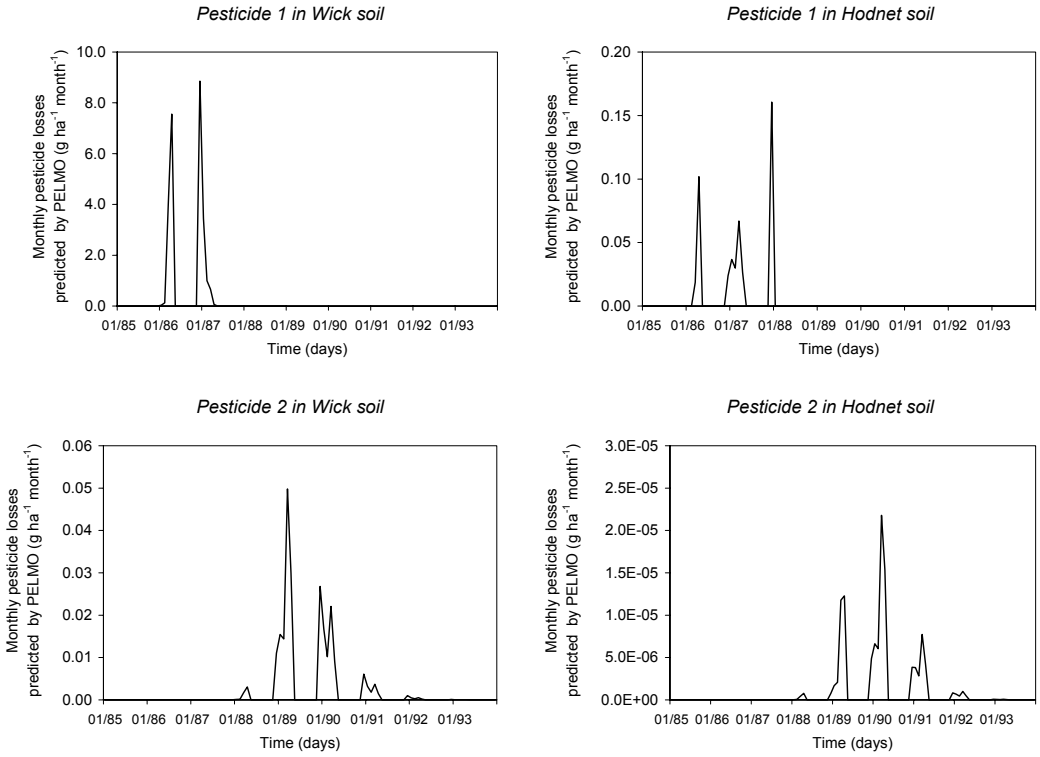

Figure 3-2. Monthly predictions for pesticide losses by PELMO for the four base-case scenarios.

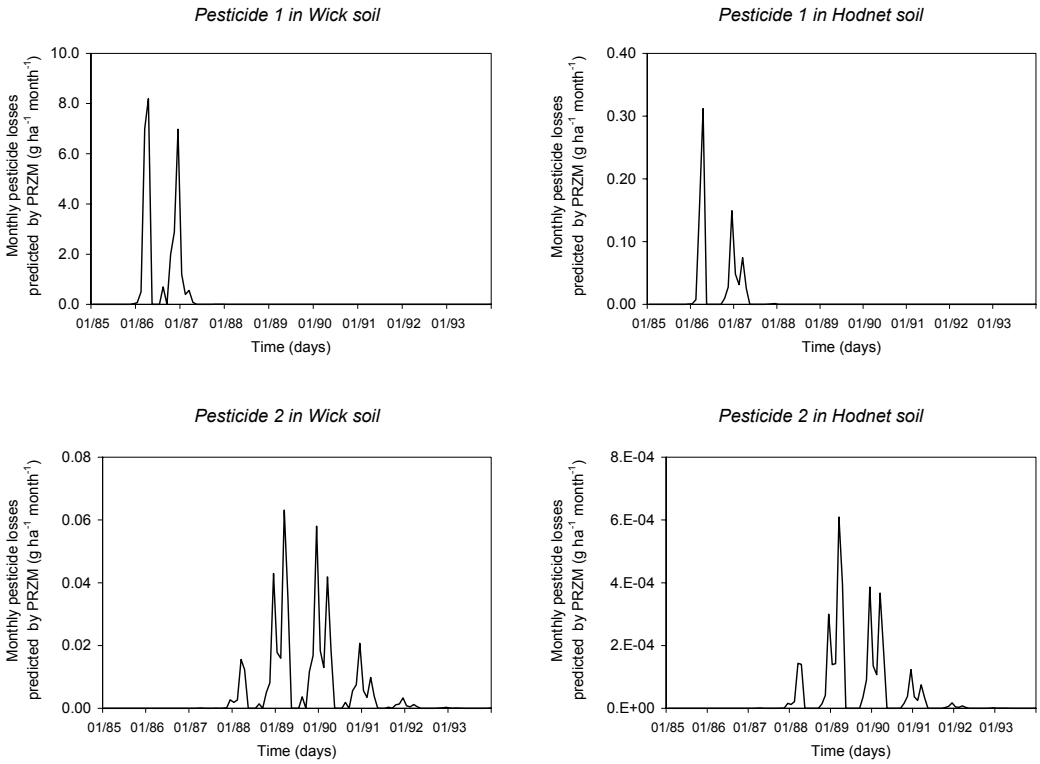

Figure 3-3. Monthly predictions for pesticide losses by PRZM for the four base-case scenarios.

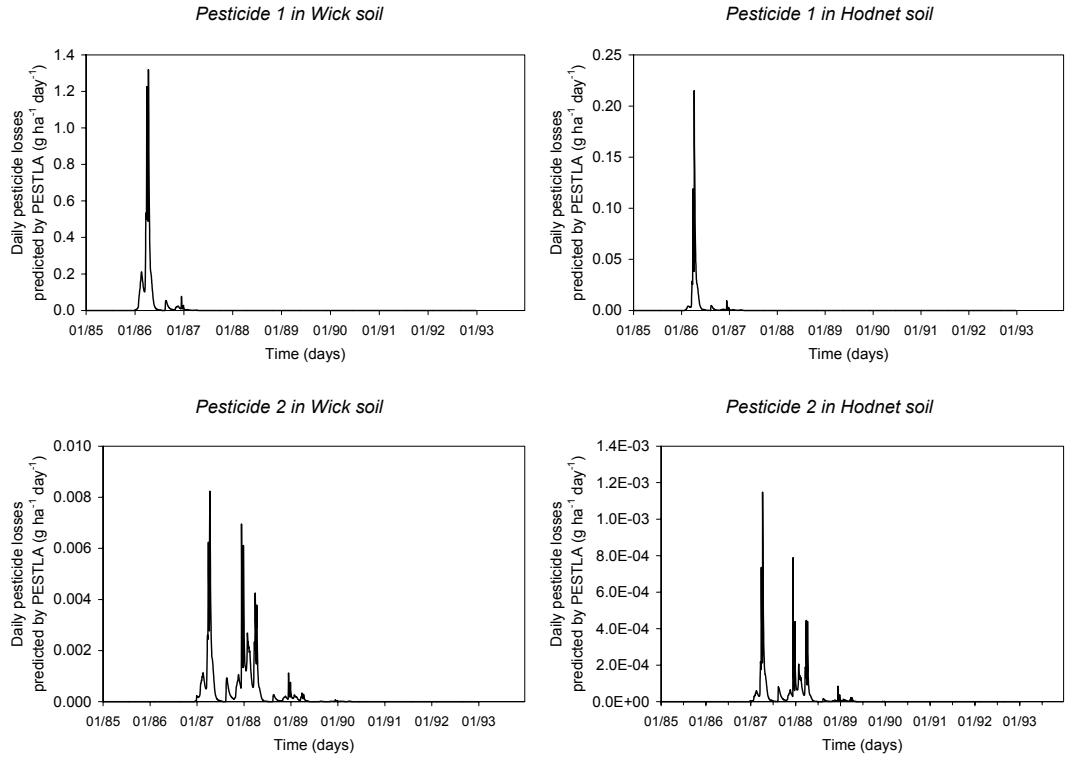

Figure 3-4. Daily predictions for pesticide losses by PESTLA for the four base-case scenarios.

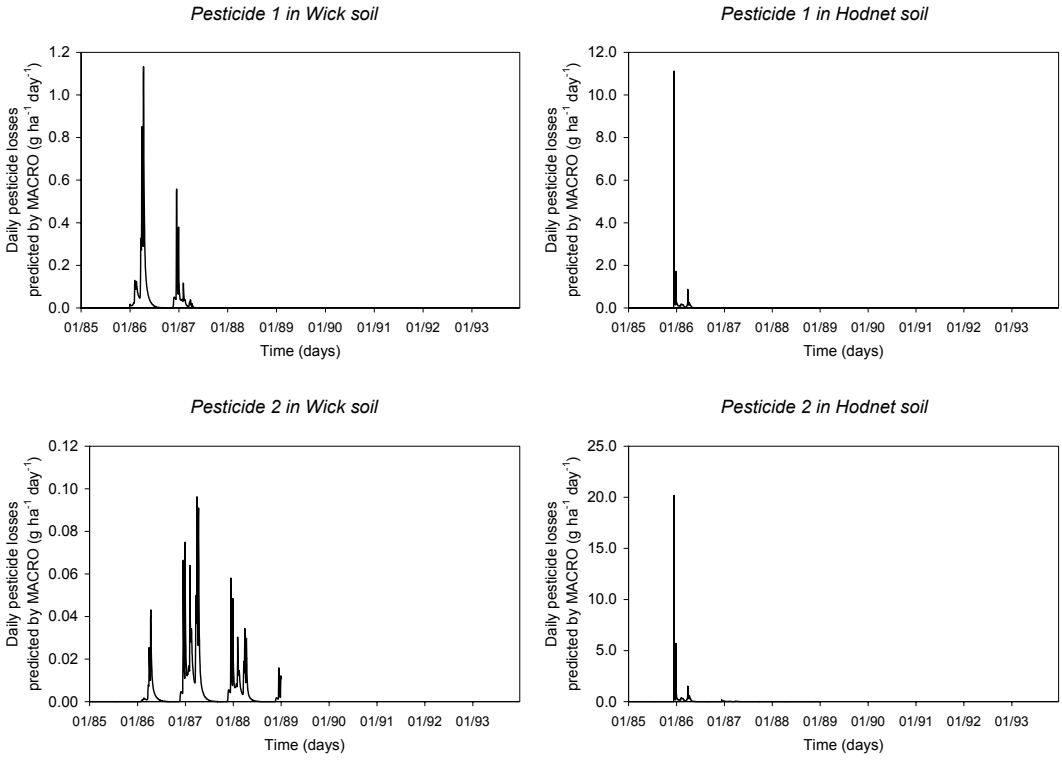

Figure 3-5. Daily predictions for pesticide losses by MACRO for the four base-case scenarios.

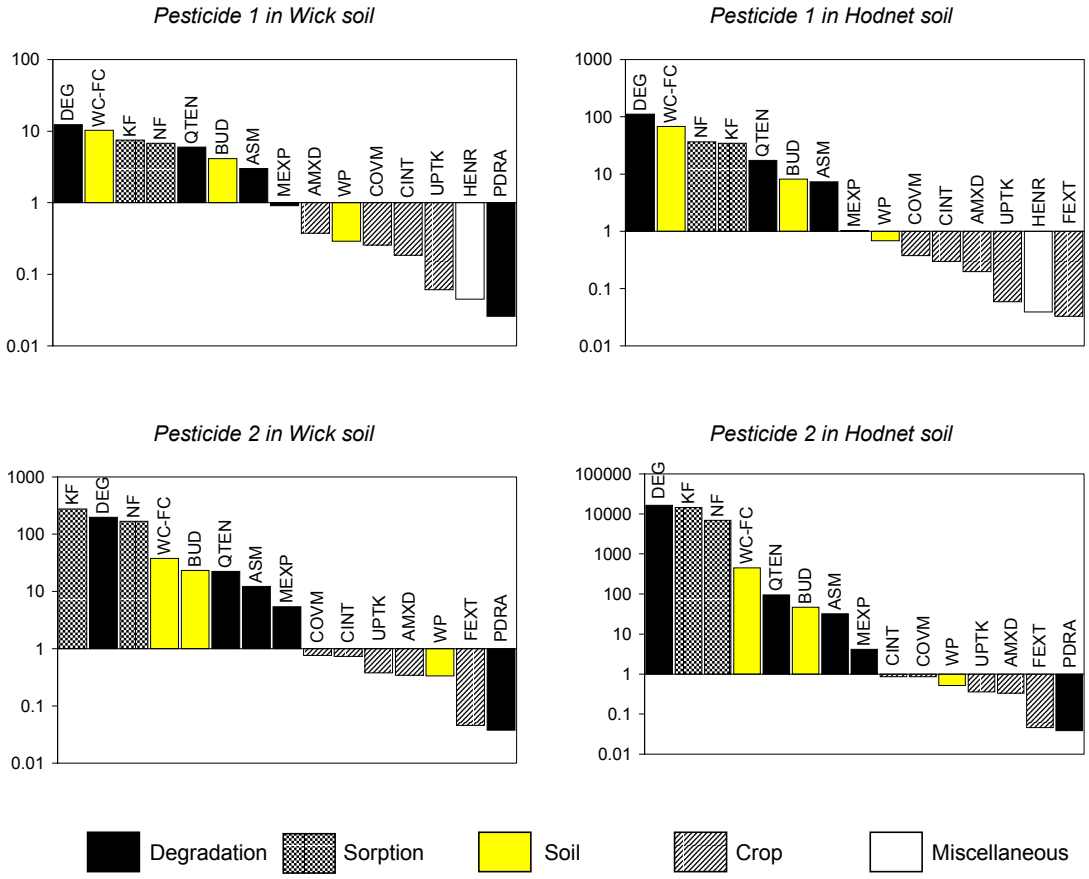

Figure 3-6. Sensitivity results for PELMO to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 3-1.

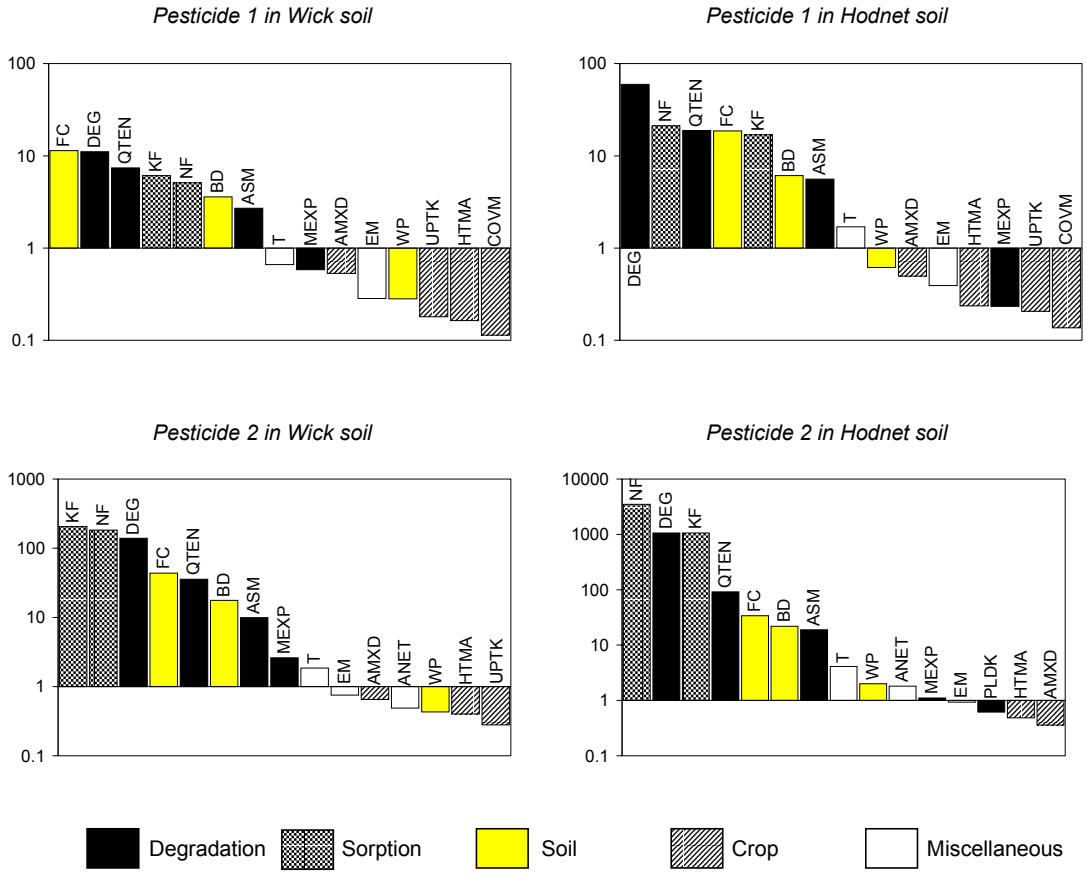

Figure 3-7. Sensitivity results for PRZM to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 3-2.

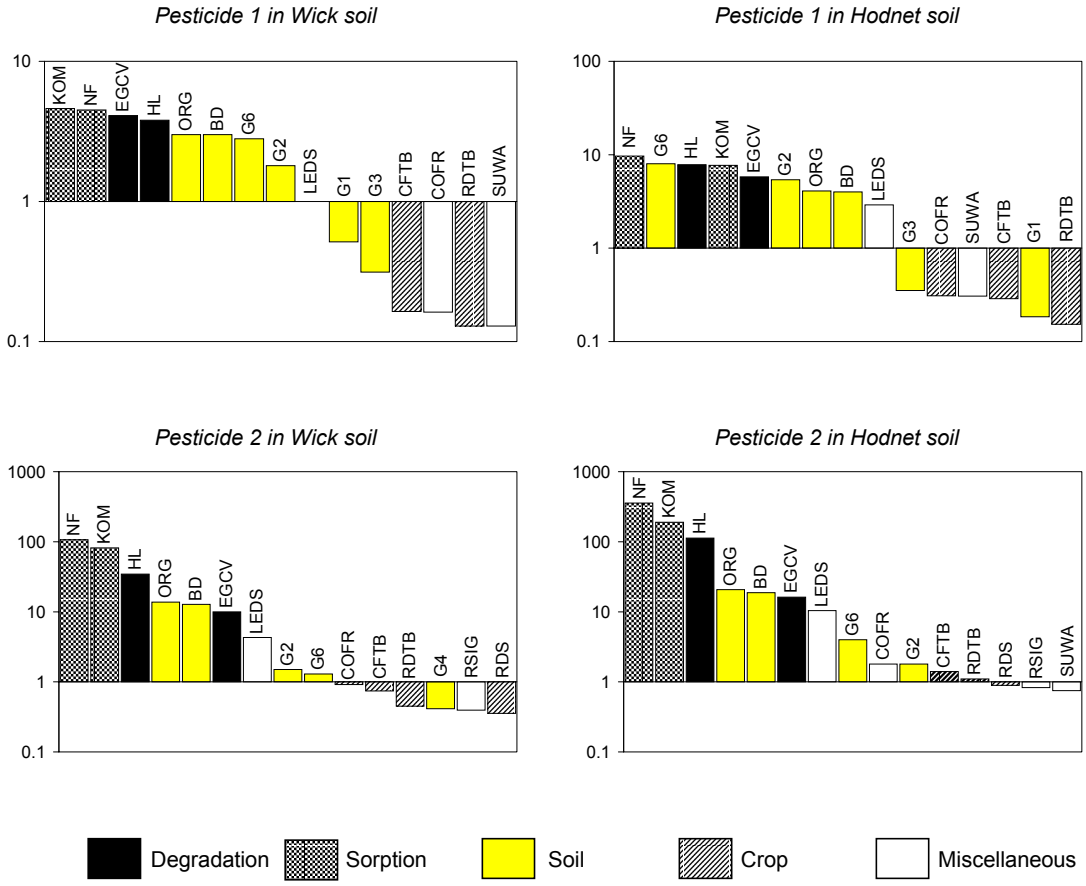

Figure 3-8. Sensitivity results for PESTLA to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 3-3.

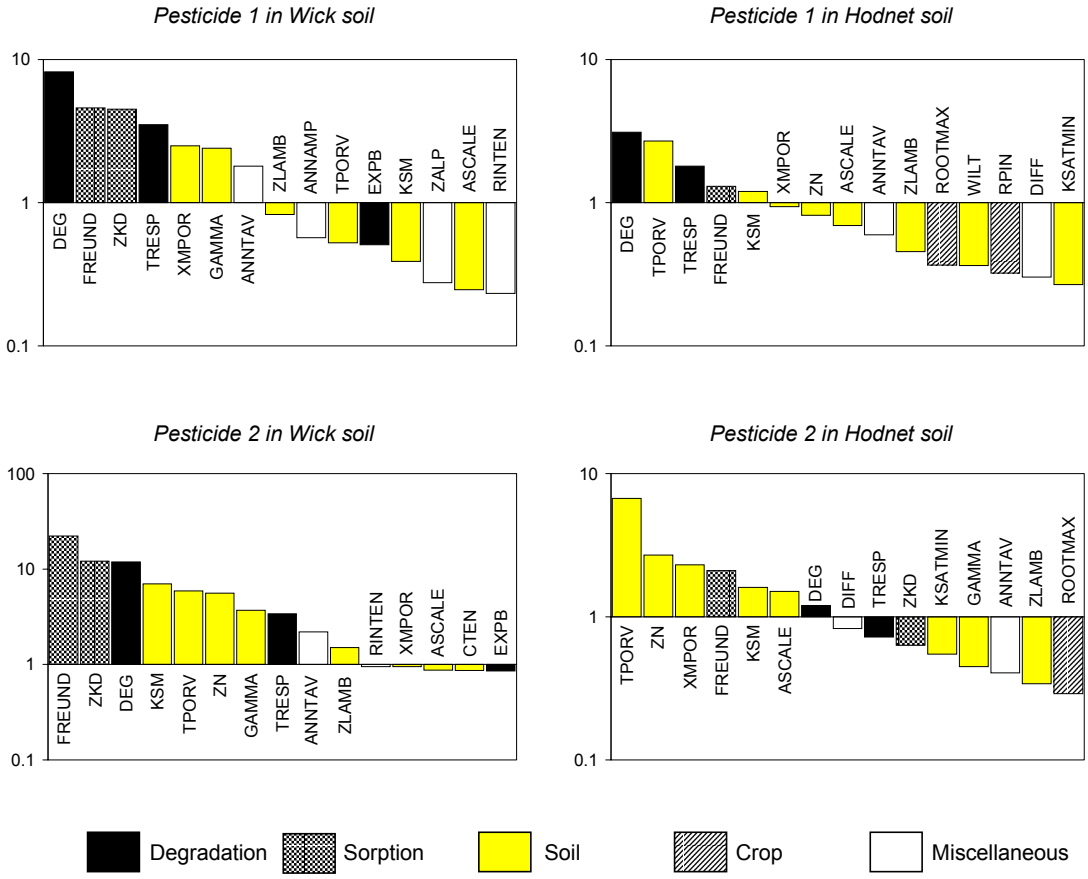

Figure 3-9. Sensitivity results for MACRO to predictions of pesticide losses. Parameters have been ranked by decreasing MAROV values (decreasing sensitivity). A brief description of the parameters can be found in Appendix 3-4.

Chapter 4

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 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. The scenario dependence observed suggests that a dedicated sensitivity analysis may need to be undertaken for each modelling exercise. 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,

Dubus I.G. & Brown C.D. (2002). Sensitivity and first-step uncertainty analyses for the preferential flow model MACRO. *Journal of Environmental Quality*, 31:227-240.

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 over-estimated 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.

INTRODUCTION

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 & 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 & 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.*, 2000a). 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 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 groundwater 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 chemical to depth followed by lateral transport by artificial drains (Brown *et al.*, 2000b). MACRO has been coupled to one of the European scenarios to estimate leaching of pesticides to groundwater 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 parameterisation and in the selection of parameters for calibration and probabilistic modelling. Knowing which model inputs most influence model predictions can also help in the assessment of the quality of a modelling study and in the prioritisation 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 which 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 characterised by a flow rate and solute concentration (Jarvis, 1994). Soil water flow and solute transport in the micropores is modelled using Richards' equation and the convection-dispersion equation, respectively, whilst 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 which 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 modelled 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 behaviour. 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 & Jarvis, 1994). Despite the widespread interest in using MACRO, the model remains difficult to parameterise (Brown *et al.*, 2000b). 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.

Parameterisation 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 (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 modelling scenarios with different running times was still meaningful.

Soils which 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 4-1 and 4-2. Water retention data were measured using the standard methods for England and Wales (Avery & 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 1-m depth are used as a protective indicator for concentrations in groundwater.

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 & 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, whilst 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 & 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 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 days at 20°C (equivalent to a half-life of 20 days at 8°C). Pesticide 2 has a K_{oc} of 100 ml g^{-1} and a laboratory half-life in soil of 23.3 days at 20°C (equivalent to a half-life of 60 days at 8°C). Sorption of the two pesticides was assumed to be characterised 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 & Bardon, 1998) showed that these properties were realistic (Figure 4-1). The parameter 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.s. ha^{-1} on 1 November of the first year of simulation. The simulated crop was winter wheat 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 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 1-m depth for the sandy loam and the 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 in 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 pre-defined 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 & Dowlatabadi, 1994), in contrast to the conceptually simpler one-at-a-time sensitivity analysis. Secondly, they are relatively simple to conduct when using appropriate

software (Hamby, 1995). Thirdly, the use of an efficient sampling scheme (such as the Latin Hypercube sampling; McKay *et al.*, 1979) greatly decreases the number of runs required. Fourthly, 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 which concentrated *a priori* on the most sensitive parameters (*e.g.* Boesten & van der Linden, 1991), the number of input parameters considered for variation here was maximised. Where little information is available on the sensitivity of the model, good confidence in the sensitivity results may be jeopardised 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 modelling 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 4-3 and 4-4 present the list of parameters which 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:

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

where O is the output value,

O_{BC} is the output value for the base case scenario,

I is the input value,

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 which enables the

number of runs to be kept to a minimum (Blower & 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 standardised (*i.e.* the population mean was subtracted from the individual results and the resulting difference was divided by the standard deviation of the population) and then ranked. The standardisation 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 non-linearity on the assessment of sensitivity (Iman & Conover, 1979). Standardised and ranked model predictions for pesticide losses were related to standardised 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 standardised model output,

X_i is a standardised input parameter,

b_i is the regression coefficient for each X_i,

ε is the regression error,

k is the number of input parameters varied in the sensitivity analysis.

The magnitude of the regression coefficients of the regression (or Standardised 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 modelling 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 4-5. Percolation for the two soils was very similar, with a difference of 12-13 mm in the annual predicted volumes of water. Smaller percolation volumes were predicted 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 (viz. 10.5 days) 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% 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 to 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 & 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 4-2 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.s. 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 whilst 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 which were varied had an influence on the MACRO predictions for volumes of water percolated at 1-m depth. Table 4-6 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 which 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 prerun period to allow the model to equilibrate was included in the modelling.

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 characterised 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) analysed 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 to 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 4-7) 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 4-3 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 & 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 influence as compared to the sandy loam, especially for the scenario describing the leaching of Pesticide 2. The parameter which 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 which 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 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 which are prone to preferential flow, parameters which 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 & 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 standardised rank regression coefficient are presented in Table 4-8. 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 which 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 which did not match the variation of the input parameters in the one-at-a-time sensitivity analysis. Secondly, parameters were all varied at the same time in the Monte Carlo approach compared to the single parameter variation in the one-at-a-time sensitivity analysis. Thirdly, the derivation of the SRRC coefficients in the Monte Carlo approach relies on a linear regression between ranked values for pesticides losses and ranked values for input parameters. Results for standardised data clearly showed that the system considered was non-linear (r^2 0.68-0.90 for the four scenarios). It is thus questionable whether the investigation of the sensitivity of non-linear 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 which 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 4-4 and 4-5 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

Figure 4-4 suggests that the base-case water retention 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 followed was to investigate the sensitivity of MACRO, results can be used as a first step assessment of the uncertainty associated with the modelling. This assessment was made possible because parameters were varied within a range which reflected their uncertainty. Box plots showing the distribution of the predictions for pesticide losses for the four scenarios are presented in Figure 4-6. The maximum variation in the prediction of pesticide losses by MACRO was observed for the Pesticide 1 on 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 characterised by high uncertainty (Wolt, 1999). Predictions related to the largest losses were only attributed to a few runs which 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 25^{th}- and 75^{th}-percentile are therefore more appropriate to characterise the uncertainty. Coefficients of variation (CV's) for pesticide losses ranged from 60% (Pesticide 1 on Hodnet) to 150% (Pesticide 2 on Wick) and were in sharp contrast with CV's 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 4-5). 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 sensitive parameters as identified in this study and that the resulting variability in model predictions will be less.

Implications for Modelling 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 recognised 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 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 characterised 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 sub-routines 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 sub-routines, particularly in those instances where parameters have been shown to be particularly sensitive.

Detailed ranking of input parameters (Tables 4-6 and 4-7) is expected to have a number of applications in modelling with MACRO. First, the information can be used to guide parameterisation efforts and identify those parameters whose values require the most (or the least) time and financial resources for their determination. Secondly, the information can assist when selecting parameters for adjustment when calibrating the model to experimental data, either manually or by inverse modelling. The third application of these results relates to probabilistic modelling. The probabilistic approach to modelling recognises the uncertainty associated with input parameters and aims at propagating it through the modelling 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 which 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 in the winter), it is recommended that a rapid sensitivity analysis is carried out to confirm those parameters which most influence model predictions. This scenario-based sensitivity analysis might concentrate on, say, the 10-15 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 modelling 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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Table 4-1. Selected properties of the Wick and Hodnet soils.

Depth	Org. 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 4-2. 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

Table 4-3. Model parameterisation for Pesticides 1 and 2 on 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
	Parameterisation 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	4.50E1
BETA	Root adaptability factor (-)	0.2	0.1	0.4	Log-normal	4.50E-3
CANCAP	Canopy Interception Capacity (mm)	2	1	4	Log-normal	4.50E-1
CFORM	Form factor (-)	1.7	1.3	2	Normal	2.34E-2
CRITAIR	Critical soil air content for root water uptake (%)	5	2	8	Normal	2.34
CTEN †	Boundary soil water tension (cm)	10	5	20	Log-normal	1.12E1
DFORM	Form factor (-)	0.7	0.5	0.8	Normal	2.60E-3
DIFF	Diffusion coefficient in water ($m^2\ s^{-1}$)	4.6E-10	1E-10	1E-09	Normal	3.53E-20
DV	Dispersivity (cm)	1	0.2	5	Log-normal	6.26E-1
EXPB	Exponent moisture relation (-)	0.70	0.42	0.98	Normal	2.04E-2
FEXT	Canopy wash-off coefficient (mm^{-1})	0.01	0.005	0.02	Log-normal	1.12E-5

FRACMAC	Fraction sorption sites in macropores (-)	0.02	0.005	0.1	Log-normal	1.82E-4
FREUND	Freundlich exponent (-)	0.9	0.72	1.08	Normal	8.43E-3
GAMMA †	Bulk density (g cm^{-3})	1.35	1.21	1.48	Normal	4.74E-3
KSATMIN †	Saturated hydraulic conductivity (mm h^{-1})	120	30	480	Log-normal	1.62E3
KSM †	Boundary hydraulic conductivity (mm h^{-1})	0.492	0.246	0.738	Normal	1.58E-2
LAIHAR	Leaf Area Index at harvest (-)	1	0.5	2	Log-normal	1.12E-1
LAIMAX	Maximum Leaf Area Index (-)	6.2	5.2	7.2	Normal	2.60E-1
LAIMIN	Leaf Area Index at zdatemin (-)	1	0.5	2	Normal	6.51E-2
RINTEN	Rainfall intensity (mm h^{-1})	2	1	4	Log-normal	4.50E-1
ROOTINIT	Root Depth at zdatemin (m)	0.2	0.1	0.4	Normal	2.60E-3
ROOTMAX	Maximum root depth (m)	0.8	0.6	1	Normal	1.04E-2
RPIN	Root distribution (%)	70	60	80	Normal	2.60E1
TEMPINI †	Initial soil temperature (°C)	8	6	10	Normal	1.04
THETAINI †	Initial soil moisture (%)	27.75	20.81	34.69	Normal	1.25E1
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	1.04E-4
WATEN	Critical water tension for root water uptake (m)	5	1	20	Uniform	-

WILT †	Wilting point (%)	10.54	9.486	11.594	Normal	2.89E-1
XMPOR †	Boundary soil water content (%)	35.71	32.14	39.28	Normal	3.32
ZALP	Correction factor for wet canopy evaporation (-)	1	1	1.3	Uniform	-
ZFINT	Fraction of irrigation intercepted by canopy (-)	0.1	0.05	0.2	Log-normal	1.12E-3
ZHMIN	Crop height at zdatemin (m)	0.15	0.1	0.2	Normal	6.51E-4
ZLAMB †	Pore size distribution index (-)	0.163	0.082	0.326	Log-normal	2.99E-3
ZM †	Tortuosity factor micropores (-)	0.5	0.25	1	Log-normal	2.81E-2
ZMIX	Mixing depth (mm)	1	0.25	20	Log-normal	4.54E-1
ZN †	Pore size distribution factor for macropores (-)	4.40	3.96	4.84	Normal	5.16E-1
	Parameterisation specific to Pesticide 1					
CANDEG	Canopy degradation rate (d^{-1})	0.0893	0.0446	0.1786	Log-normal	8.97E-4
DEG †	Degradation rates (d^{-1})	0.0893	0.0447	0.1786	Log-normal	8.97E-4
ZKD †	Sorption coefficient ($cm^3\ g^{-1}$)	0.34	0.17	0.68	Log-normal	1.30E-2
	Parameterisation specific to Pesticide 2					
CANDEG	Canopy degradation rate (d^{-1})	0.0298	0.0149	0.0596	Log-normal	9.99E-5
DEG †	Degradation rates (d^{-1})	0.0298	0.0149	0.0596	Log-normal	9.99E-5
ZKD †	Sorption coefficient ($cm^3\ g^{-1}$)	1.7	0.85	3.4	Log-normal	3.25E-1

† Primary parameter to which slave parameters were linked.

Table 4-4. Model parameterisation for Pesticides 1 and 2 on 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
	Parameterisation 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	4.50E1
BETA	Root adaptability factor (-)	0.2	0.1	0.4	Log-normal	4.50E-3
CANCAP	Canopy Interception Capacity (mm)	2	1	4	Log-normal	4.50E-1
CFORM	Form factor (-)	1.7	1.3	2	Normal	2.34E-2
CRITAIR	Critical soil air content for root water uptake (%)	5	2	8	Normal	2.34
CTEN †	Boundary soil water tension (cm)	18	9	36	Log-normal	3.64E1
DFORM	Form factor (-)	0.7	0.5	0.8	Normal	2.60E-3
DIFF	Diffusion coefficient in water ($m^2\ s^{-1}$)	4.6E-10	1E-10	1E-09	Normal	3.53E-20
DV	Dispersivity (cm)	1	0.2	5	Log-normal	6.26E-1
EXPB	Exponent moisture relation (-)	0.70	0.42	0.98	Normal	2.04E-2
FEXT	Canopy wash-off coefficient (mm^{-1})	0.01	0.005	0.02	Log-normal	1.12E-5

FRACMAC	Fraction sorption sites in macropores (-)	0.02	0.005	0.1	Log-normal	1.82E-4
FREUND	Freundlich exponent (-)	0.9	0.72	1.08	Normal	8.43E-3
GAMMA †	Bulk density (g cm^{-3})	1.39	1.25	1.52	Normal	5.03E-3
KSATMIN †	Saturated hydraulic conductivity (mm h^{-1})	39.2	19.6	78.5	Log-normal	1.73E2
KSM †	Boundary hydraulic conductivity (mm h^{-1})	0.088	0.044	0.132	Normal	5.04E-4
LAIHAR	Leaf Area Index at harvest (-)	1	0.5	2	Log-normal	1.12E-1
LAIMAX	Maximum Leaf Area Index (-)	6.2	5.2	7.2	Normal	2.60E-1
LAIMIN	Leaf Area Index at zdatemin (-)	1	0.5	2	Normal	6.51E-2
RINTEN	Rainfall intensity (mm h^{-1})	2	1	4	Log-normal	4.50E-1
ROOTINIT	Root Depth at zdatemin (m)	0.2	0.1	0.4	Normal	2.60E-3
ROOTMAX	Maximum root depth (m)	0.8	0.6	1	Normal	1.04E-2
RPIN	Root distribution (%)	70	60	80	Normal	2.60E1
TEMPINI †	Initial soil temperature (°C)	8	6	10	Normal	1.04
THETAINI †	Initial soil moisture (%)	27.75	20.81	34.69	Normal	1.25E1
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	1.04E-4
WATEN	Critical water tension for root water uptake (m)	5	1	20	Uniform	-

WILT †	Wilting point (%)	16.80	15.12	18.48	Normal	7.35E-1
XMPOR †	Boundary soil water content (%)	38.74	34.87	42.61	Normal	3.91
ZALP	Correction factor for wet canopy evaporation (-)	1	1	1.3	Uniform	-
ZFINT	Fraction of irrigation intercepted by canopy (-)	0.1	0.05	0.2	Log-normal	1.12E-3
ZHMIN	Crop height at zdatemin (m)	0.15	0.1	0.2	Normal	6.51E-4
ZLAMB †	Pore size distribution index (-)	0.084	0.042	0.168	Log-normal	7.94E-4
ZM †	Tortuosity factor micropores (-)	0.5	0.25	1	Log-normal	2.81E-2
ZMIX	Mixing depth (mm)	1	0.25	20	Log-normal	4.54E-1
ZN †	Pore size distribution factor for macropores (-)	4.92	3.35	6.49	Normal	6.45E-1
	Parameterisation specific to Pesticide 1					
CANDEG	Canopy degradation rate (d^{-1})	0.0893	0.0446	0.1786	Log-normal	8.97E-4
DEG †	Degradation rates (d^{-1})	0.0893	0.0447	0.1786	Log-normal	8.97E-4
ZKD †	Sorption coefficient ($cm^3\ g^{-1}$)	0.230	0.115	0.460	Log-normal	5.95E-3
	Parameterisation specific to Pesticide 2					
CANDEG	Canopy degradation rate (d^{-1})	0.0298	0.0149	0.0596	Log-normal	9.99E-5
DEG †	Degradation rates (d^{-1})	0.0298	0.0149	0.0596	Log-normal	9.99E-5
ZKD †	Sorption coefficient ($cm^3\ g^{-1}$)	1.150	0.575	2.300	Log-normal	1.49E-1

† Primary parameter to which slave parameters were linked.

Table 4-5. Annual and accumulated water percolation and pesticide losses for the four base-case scenarios.

	Water percolation				Pesticide losses			
	Wick		Hodnet		Wick		Hodnet	
Year	Pest. 1	Pest. 2	Pest. 1	Pest. 2	Pest. 1	Pest. 2	Pest. 1	Pest. 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

Table 4-6. Classification of MACRO input parameters according to their influence on the prediction of accumulated water percolated to 1-m depth (one-at-a-time approach). Parameters are classified by decreasing influence according to their MAROV value. A brief description of the parameters is provided in Table 4-3.

	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

Table 4-7. Classification of MACRO input parameters according to their influence on the prediction of pesticide losses at 1-m depth (one-at-a-time approach). Parameters are classified by decreasing influence according to their MAROV value. A brief description of the parameters is provided in Table 4-3.

	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

Table 4-8. Classification of MACRO input parameters according to their influence on the prediction of pesticide losses at 1-m depth (Monte-Carlo approach). Parameters are classified by decreasing influence according to their SRRC value. A brief description of the parameters is provided in Table 4-3.

	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.

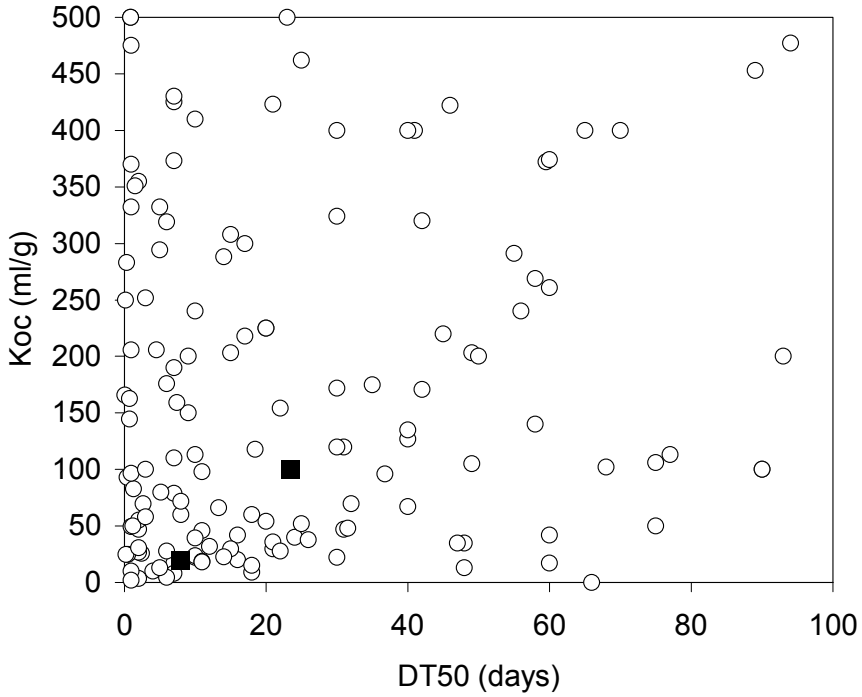

Figure 4-1. Comparison between K_{oc} and DT50 values of the two theoretical pesticides considered in the present study (closed squares) and those for pesticides registered for use in the UK (open circles). Properties for registered compounds were taken from Lewis and Bardon (1998). Only those registered pesticides with K_{oc} <500 ml/g and DT50 <100 days are shown.

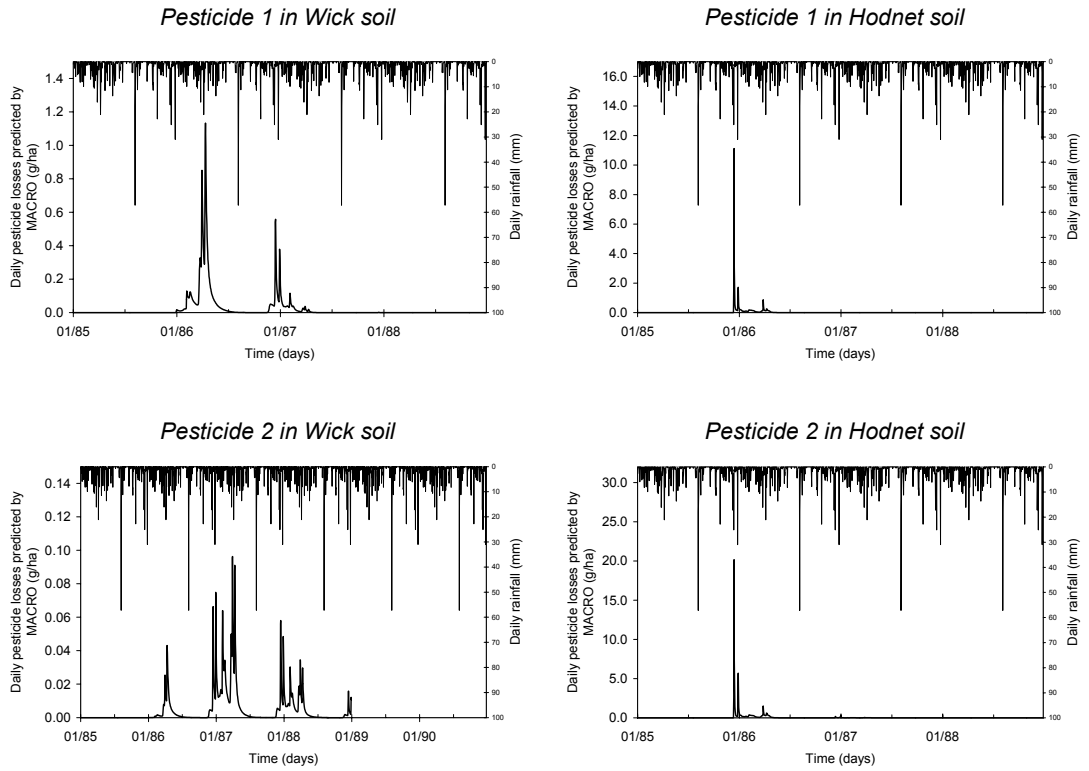

Figure 4-2. Rainfall data and pesticide leaching breakthrough at 1-m depth predicted by MACRO for the four base case scenarios.

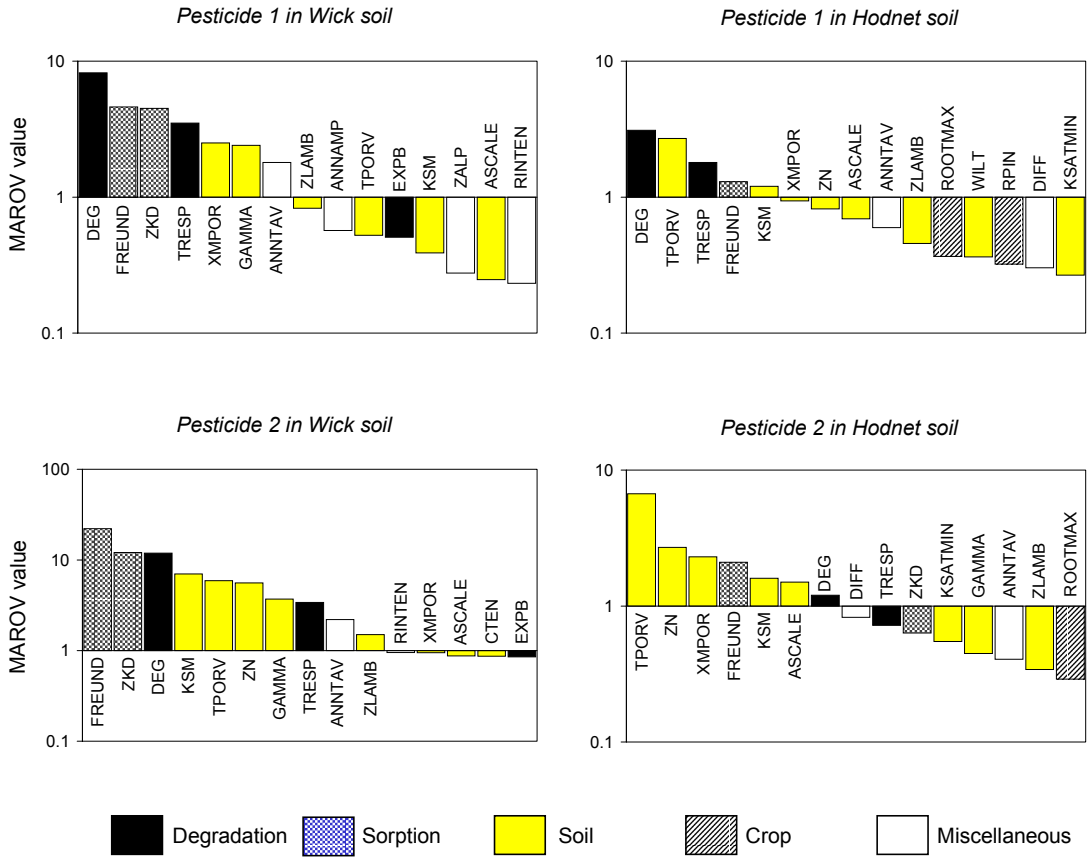

Figure 4-3. Classification into broad classes of the 15 most influential parameters for predictions of pesticide losses for the four scenarios (one-at-a-time approach). Parameters are classified by decreasing influence according to their MAROV value.

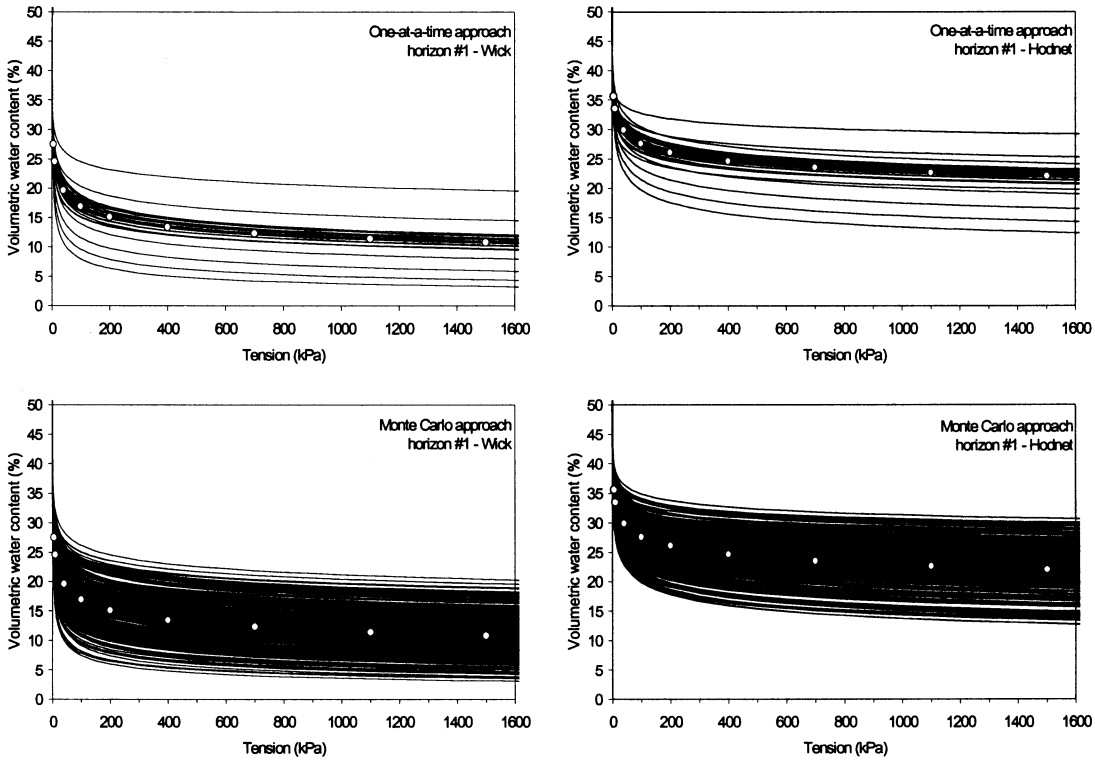

Figure 4-4. Variations of the water retention curves in the one-at-a-time (top two charts) and Monte Carlo (bottom two charts) approaches. Water retention curves generated in the sensitivity analyses (black lines) are compared to those from the base-case scenarios (open circles). All curves are modelled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

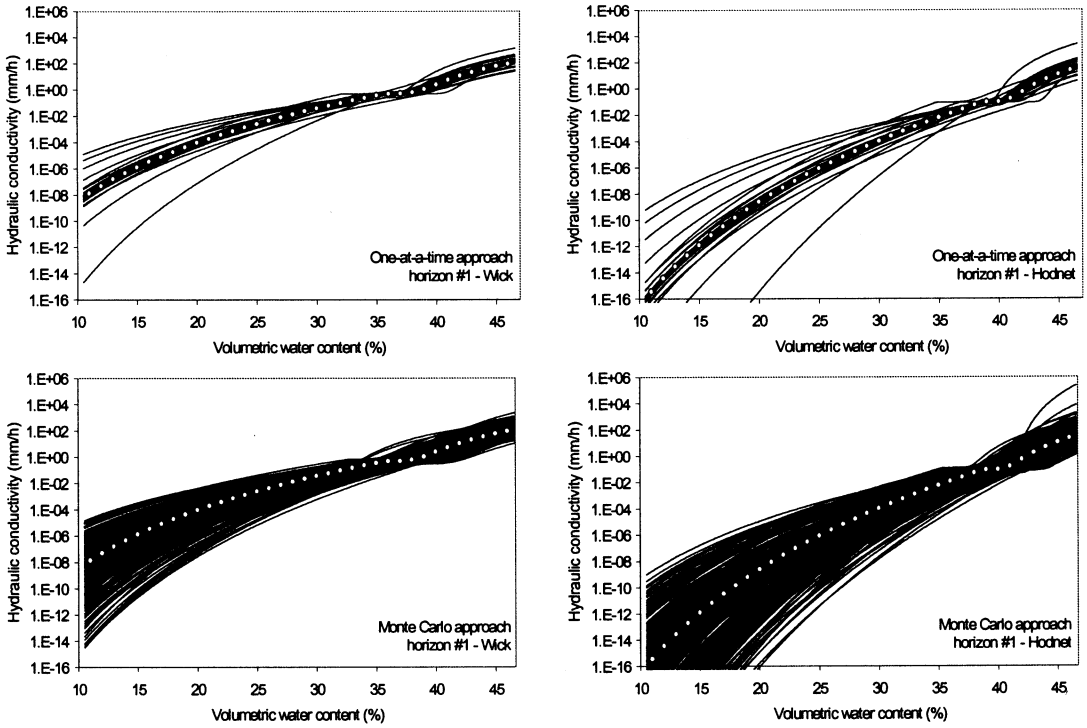

Figure 4-5. Variations of the hydraulic conductivity curves in the one-at-a-time (top two charts) and Monte Carlo (bottom two charts) approaches. Hydraulic conductivity retention curves generated in the sensitivity analyses (black lines) are compared to those from the base-case scenarios (open circles).

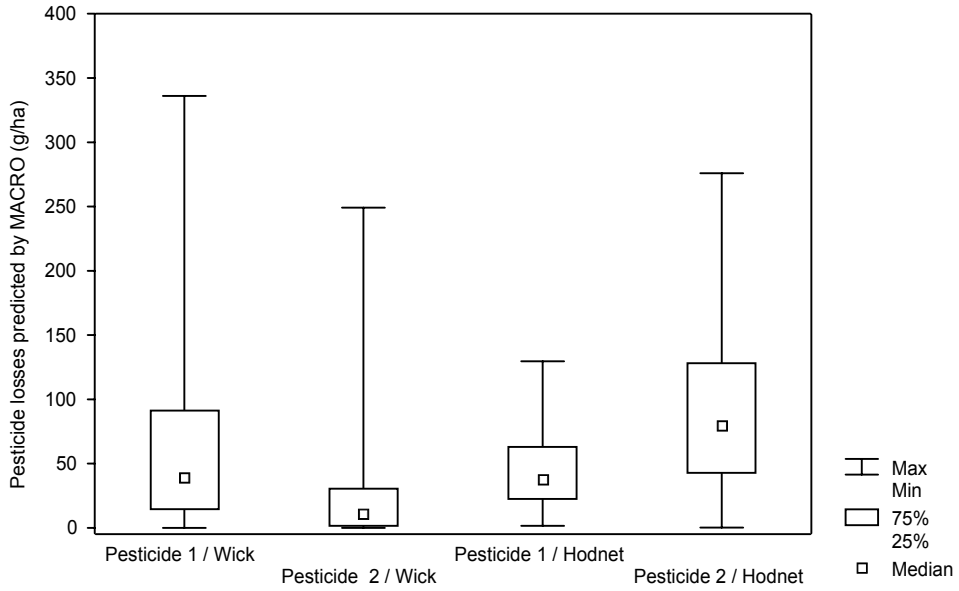

Figure 4-6. Box plots describing the distributions of predictions for pesticide losses for the four scenarios (Monte Carlo approach).

Chapter 5

INVERSE MODELLING FOR ESTIMATING SORPTION AND DEGRADATION PARAMETERS FOR PESTICIDES. PART 1: DATASETS AND INITIAL CALIBRATIONS

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ABSTRACT

Sorption and degradation parameters derived from laboratory experiments are traditionally used to predict the fate of agrochemicals under outdoor conditions. There is, however, evidence that these parameters may not always be applicable to the description of field situations. Inverse modelling consists in adjusting selected model input parameters until the fit between model outputs and laboratory or field observations is optimised in the weighted least squares sense. Although the technique is widely used in groundwater modelling, the combination of inverse modelling with pesticide fate models has rarely been investigated. In this first paper of a two-part series, we report on the combination of the inverse modelling package PEST with the leaching model PESTRAS to derive sorption and degradation parameters using data from seven lysimeters on pesticide leaching. Optimised values for Kom and DT50 ranged from 8.2 to 37.9 ml/g and from 11.0 to 32.4 days,

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respectively. These values were within the variation range reported in laboratory experiments. Improvements in the simulation of pesticide concentrations and cumulative leaching loads were achieved in most cases relative to the use of median values. Inverse modelling potentially provides a means to improve model performance, to back-calculate key model inputs from field data and to generate valuable information on the behaviour of pesticide leaching models.

INTRODUCTION

Mathematical modelling has been increasingly used in the last two decades to describe and predict the fate of agrochemicals in the environment, particularly the transfer of compounds to surface waters and groundwater. Compared to standard field studies, the use of pesticide fate models is cost- and time-effective and does not rely on rainfall and other environmental factors to yield results of interest. Furthermore, it offers the possibility of encompassing the variability of weather conditions through the use of long-term data series and offers some extrapolation capabilities to other climates, soils and cropping practices. As a result of the numerous benefits of modelling, a large number of models have been developed, contrasting in their complexity, parameter requirements and their intended use. The increasing importance of pesticide fate modelling was confirmed in the European Council directive 91/414/EEC (European Community, 1991) which regulates the placing of plant protection products on the European market.

Sorption and degradation parameters are traditionally those which have the largest influence on pesticide output (*i.e.* maximum concentrations predicted, total losses) from pesticide leaching models (Boesten, 1991; Tiktak *et al.*, 1994; Dubus & Brown, 2002; Dubus *et al.*, 2002a). Since sorption and degradation processes cannot be measured independently in the field, the parameters required are traditionally determined through laboratory experiments under controlled conditions using a range of soils. However, there are doubts in some instances on the validity of the use of laboratory values to describe pesticide fate under outdoor conditions (Walker &

Jurado-Exposito, 1998; Beulke *et al.*, 2000). Innovative laboratory methods that attempt to reproduce field conditions more closely have been investigated (Gaillardon *et al.*, 1991; Kookana, 1998), but no method has been accepted yet and sorption and degradation parameters derived under controlled laboratory conditions are still very much in use. An alternative which may appear promising is the use of data collected during field or lysimeter experiments to determine those parameters. This can be achieved through calibration of a pesticide leaching model for sorption and degradation parameters against concentrations of pesticide in leachate or soil residues measured under outdoor conditions. Automatic calibration of a model against experimental data by varying model parameters has been used extensively in groundwater hydrological modelling (Poeter & Hill, 1997) and is referred to as inverse modelling. The method can be used to determine reasonable values for model input parameters which are difficult to measure and that have been shown to have a large influence on model output. As well as being sensitive in determining leaching losses of pesticides, degradation and sorption parameters are largely uncertain (Dubus *et al.*, 2002a). Application of the inverse modelling approach for their determination thus deserves investigation.

An evaluation of the combination of the inverse modelling package PEST with the leaching model PESTRAS (PESticide TRansport ASsessment) was undertaken. The present paper reports on the simulation of leaching of a herbicide from seven lysimeters and on the possibility to derive sorption and degradation parameters from lysimeter data.

MATERIALS AND METHODS

Soils and lysimeter experiments

As part of the regulatory submission for a contact herbicide, seven lysimeter experiments using sandy loam soils were conducted in Germany following the BBA guideline (BBA, 1990). Sand contents in the top 30/40 cm were 68, 76 and 54% for

Borstel, Schifferstadt and Landau soils, respectively, whilst organic matter content ranged from 1.5 to 2.7% . The lysimeters, which ranged from 1- to 1.2-m in depth, were cropped and managed according to good agricultural practice. The surface area was 1 m^2. The ^{14}C-herbicide was applied to all lysimeters as a water soluble formulation between the end of March and beginning of July at application rates ranging from 0.45 to 1.35 kg/ha. Some lysimeters had to be irrigated to meet the German BBA guideline for lysimeter studies (annual rainfall > 800 mm). Leachate from the lysimeters was sampled at irregular intervals and analysed for total radioactivity by liquid scintillation counting and for concentrations of the herbicide by thin layer chromatography and/or GC-MS. Table 5-1 presents additional information on the seven lysimeters.

PESTRAS modelling

The PESTRAS model (Tiktak *et al.*, 1994) was used in its version 3.1.3 to simulate water and herbicide movement through the lysimeters using site-specific weather data. PESTRAS is a one-dimensional multi-layer model that includes subroutines on water and solute transport, sorption, transformation, volatilization and plant uptake of solutes. Water and solute transport are based on the Richards' and convection-dispersion equations, respectively. Pesticide degradation is assumed to follow first-order kinetics and sorption is considered to be instantaneously at equilibrium and to be described by a Freundlich isotherm. The PESTRAS model has been evaluated against data for a sandy soil at Vredepeel in the Netherlands and showed good capabilities in predicting the leaching of bromide and two herbicides in the field when site-specific parameter values were used (Tiktak *et al.*, 1998).

For the present exercise, hydrological parameters required by PESTRAS were obtained by fitting the van Genuchten equation (Van Genuchten, 1980) where measured water release curves were available. Alternatively, data were obtained from those given for eight textural classes by Tiktak *et al.* (1996) using data for the Dutch "Winand Staring soil series" and the Dutch "old soil series". The soil classes were selected on the basis of the measured clay, silt and organic matter content.

PESTRAS does not include an explicit lysimeter bottom boundary condition. Following suggestions from the model author, the bottom boundary was set to "free drain" and the parameter α of the van Genuchten equation was fixed to 100 times the value estimated for the soils within the bottom 10 cm of the profile. With these settings, outflow only occurs when the bottom layer is virtually saturated and thus reflects the specific conditions in zero-suction lysimeters.

The crops grown in the seven lysimeters are listed in Table 5-1. The time-course of leaf area indices for cereals was taken from Dikau (1986) and Knisel (1980) and adapted to the actual sowing and harvest dates. Leaf area indices given by Hough (1990) were used as a basis for simulating winter oilseed rape and peas and crop growth stages were used to derive the interception of the application solution by the crops. Since some soils were cultivated to *ca.* 20 cm depth at the end of each vegetation period or shortly before sowing the subsequent crop, the ploughing option of PESTRAS was used. This enabled uniform redistribution of pesticide residues in the plough layer at the end of each season. Crop parameters that influence evapotranspiration were calibrated manually within reasonable limits ("trial and error calibration") to achieve a good agreement between measured and observed volumes of leachate.

Equilibrium sorption in PESTRAS is simulated using the Freundlich equation:

$$X = Kf \times C_e^{\,nf} \quad [1]$$

where X is the amount of compound sorbed (kg/kg),

Kf is the Freundlich sorption distribution coefficient ($m^{3/n}/kg^{1/n}$),

C_e is the concentration of the compound in solution at equilibrium (kg/m^3),

nf is the Freundlich exponent.

In PESTRAS, Kf is estimated from the Freundlich sorption distribution coefficient normalised to organic matter (Kom) using the following equation:

$$Kf = f_{om} \times Kom * C_r^{\,1-nf} \quad [2]$$

where f_{om} is the mass fraction of soil organic matter (kg/kg),

C_r is the concentration at which the equilibrium concentration has been estimated (reference concentration; kg/m^3).

No data specific to the lysimeters on sorption and degradation of the herbicide were available. In the first instance, sorption (the sorption distribution coefficient normalised to organic matter Kom and the Freundlich exponent nf) and degradation (the time for 50% of the pesticide to degrade in an incubation experiment as derived by first-order kinetics, DT50) parameters were set to median values as calculated from 11 sorption and 21 degradation experiments (Table 5-2). The half-life used (DT50=17.8 days at 20°C) was larger than the median of 10 field persistence studies (DT50=12.5 days). Henry's constant was set to zero as no significant loss of this herbicide through volatilisation has been reported previously. In a second stage, the two input parameters Kom and DT50 were optimised by inverse modelling.

Inverse modelling

Inverse modelling was carried out using the parameter estimation package PEST (Doherty, 2000) which implements a modified version of the Gauss-Marquardt-Levenberg non-linear estimation algorithm. PEST controls a model by communicating with it through its input and output files and will adjust selected input parameters as it runs the model repeatedly until the fit between selected output from the model and experimental data is optimised according to the weighted least squares criterion. The range of variation of parameters can be specified to avoid the return of unreasonable estimates by PEST. Since the package dialogues with model input and output files only, it can be used with virtually any command-line-driven model without the need for recoding and thus has wide applicability.

The inverse modelling exercise was limited to the calibration of Kom and DT50 which are two of the most sensitive input parameters for the PESTRAS model (Tiktak *et al.*, 1994). The Freundlich exponent nf was not included in the calibrations since Kom and nf are likely to compensate for one another in the modelling to some extent. Variations of Kom and DT50 were only restricted to

positive values by allowing the parameters to vary between 10^{-10} and 10^{10}. Target experimental values for model optimisation were herbicide concentrations in samples taken from each of the seven lysimeters. Lysimeter experiments to investigate the fate of pesticides provide a number of sampling points during the year with varying time intervals between them. Each sample is therefore an integration of pesticide leached through the soil core during the interval between two successive sampling occasions. Since PESTRAS does not offer the possibility of calculating pesticide concentrations integrated over time periods, a program was written in Perl (Perl, 2002) to compute them. Output from the Perl program was compared to experimental data by PEST at each model run to assess the goodness of fit. All sampling points were included in the dataset and concentrations below the analytical limit of quantification (0.01 μg/l) were set to half this value. Default values related to termination criteria and derivatives calculation supplied in PEST were used. Also, the same weights were assigned to all observations.

RESULTS

Water balance trial-and-error calibration

Figure 5-1 presents a comparison of measured cumulative volumes of lysimeter leachates and those simulated after calibration of PESTRAS by varying crop parameters manually in an iterative process. Overall, a good agreement between observed and simulated water balances was achieved. Identical values were used for the second and third lysimeters since they were managed in the same way and exposed to similar climatic conditions. Matching the results for the two lysimeters at the same time proved difficult as there was a considerable discrepancy between volumes of leachate for the two lysimeters (132 and 187 mm for a 10-month period for lysimeters #2 and #3, respectively). Lysimeters #4 and #5 were also run in parallel and crop parameters were hence set to identical values. The early onset of leaching in lysimeter #4 was not represented by the model, but subsequent measurements were closely matched. Lysimeters #6 and #7 are replicated lysimeters only differing in the rate of pesticide application. Although actual volumes of water

collected from these two lysimeters were relatively well matched by the model before day 390 and from day 461 onwards, an over-estimation between these two dates resulted in a large over-estimation of cumulative leachate. It was not possible to achieve a better fit by calibrating crop parameters alone.

Herbicide leaching prior to automatic calibration of Kom and DT50

Leaching of the herbicide for the seven lysimeters was first predicted by PESTRAS using the median values for Kom, nf and DT50 calculated from laboratory data. Figure 5-2 presents the observed concentrations in leachate and integrated concentrations as calculated from PESTRAS daily output. Maximum concentrations and cumulative loads over the experimental periods are presented in Table 5-3. The observed maximum concentration and cumulative loads leached through lysimeter 1 were well represented by the model prior to calibration of pesticide parameters (Table 5-3). However, the simulated timings of first breakthrough and of peak concentrations did not match those observed (Figure 5-2). Besides, the large concentration at the end of the sampling period was not simulated by the model. PESTRAS was not able to predict leaching of the herbicide through the two Schifferstadt soil lysimeters (#2 and #3) on the basis of these starting Kom and DT50 values. Large discrepancies were observed for both lysimeters, although this can be attributed to some extent to an under-estimation of water fluxes (Figure 5-1). Maximum concentrations in leachate from lysimeters #2 and #3 were under-estimated by factors of 2.6 and 1.6, respectively, but total loads were closely matched (Table 5-3). Herbicide leaching through lysimeters #4 to #7 was considerably over-estimated by the model (Table 5-3), with predicted maximum concentrations in leachate being up to 18 times larger than those observed (lysimeter 6; Figure 5-2). It is not clear why such a large discrepancy was found for this particular lysimeter.

With the exception of lysimeter #1, the model was unable to predict the maximum concentrations, patterns of leaching or cumulative loads using median sorption and degradation values even though water balances for the seven lysimeters were calibrated to some extent. The discrepancy between PESTRAS predictions and

leaching data may be attributed to i) an inadequate setting of the model input parameters affecting pesticide transport; ii) the use of sorption and degradation data which are not specific to the soils in each lysimeter; and iii) the possible failure of subroutines influencing pesticide transport in PESTRAS (*e.g.* water transport, soil temperature) to describe the fate of the herbicide in some particular lysimeters.

Herbicide leaching after calibration of Kom and DT50

Calibrated parameters obtained by inverse modelling are reported in Table 5-4. PEST supplied calibrated parameters which were different from the starting values for all seven lysimeters. None of the calibrated values for Kom and DT50 were at the upper (10^{10}) or lower (10^{-10}) limits of variation which were supplied to the inverse modelling package and calibrated values were considered reasonable. Both parameters were found to significantly influence model predictions within the inverse modelling exercise. Calibrated Kom values ranged from 8.2 to 37.9 ml/g, whilst DT50 values ranged from 11.0 to 32.4 days. In most cases, calibrated values were markedly different from the starting values, but the median of calibrated values for DT50 (17.7 days) was similar to that for laboratory values used as the initial starting value in the calibration (Table 5-2). The results, as well as the uncertainty associated with them, are within the range of variation reported for laboratory experiments (Kom range 4-102 ml/g, DT50 range 7-87 days). The variability in DT50 values determined by inverse modelling was smaller than that of laboratory values and similar to that of field data (Table 5-2). Still, considering that the lysimeter experiments were all conducted on sandy loam soils, parameter ranges obtained from inverse modelling may appear relatively large. This may be partly attributed to the natural variation inherent in lysimeter experiments. Calibrated values for Kom and DT50, to a lesser extent, were found to be significantly larger ($p<0.05$ and $p<0.10$, respectively) for lysimeters situated in Schmallenberg compared to those situated in Limburgerhof, but no relationship to the origin of the soil was noted. Differences in status and management of the lysimeters, such as weather conditions, initial soil moisture status and cropping, might have contributed to the observed relationship between calibrated parameters and experimental location.

Although 95% confidence ranges for calibrated values were relatively small for most lysimeters (Table 5-4), large correlations between the two calibrated parameters were reported in the PEST output file for most of the lysimeters (r=0.96-0.99 for 6 lysimeters). Compensating effects of parameters in the calibration as a result of large correlations may lead to situations where the solution of the inverse problem is non-unique (Poeter & Hill, 1997). Another possible indication of non-uniqueness in the calibration can be obtained by examining the ratios between the largest and smallest eigenvalues. These ratios varied between 7.5×10^{3} and 5.0×10^{7}, which suggests that combinations of Kom and DT50 may not be unique for some lysimeters. In response to these converging observations, non-uniqueness was investigated in detail for a small number of lysimeter datasets and results are presented in a companion paper (Dubus *et al.*, 2002b).

Herbicide concentrations predicted using calibrated Kom and DT50 values are compared to observed data in Figure 5-2 and maximum concentrations and loads are presented in Table 5-3. As expected, the use of calibrated parameters generated a better fit to experimental data for most of the lysimeters. The overall sum of squares reflecting the discrepancy between observed and predicted data for the seven lysimeters was reduced by a factor of 125 when using calibrated Kom and DT50 as compared to median values. The improvement in the description of experimental data was particularly evident for the second lysimeter where the data were closely matched apart from the small increase in concentrations at the end of the sampling period. In contrast, calibration gave only a slight improvement over median Kom and DT50 values for lysimeter #3 (Figure 5-2). The shape of the breakthrough curve was mis-matched by the model even with the calibrated parameters.

A number of reasons can be proposed to explain the discrepancy between observations and PESTRAS predictions for lysimeter #3 and the lack of improvement provided by the use of calibrated parameters. First, this might be attributed to the inherent variability in the analysis of pesticide concentrations at low residue levels. Although analytical determinations were carried out according to best laboratory practice in the present instance, laboratory data are always subject to

uncertainty. Secondly, some processes not included in the PESTRAS model, such as preferential flow or time dependent sorption, might significantly affect the fate of the herbicide or the mechanisms implemented into the model may be inappropriate to predict the time series of concentrations that were observed in this lysimeter. Thirdly, other parameters not included in the calibration exercise, especially those which greatly influence model predictions, may be vital in describing the breakthrough curve shown in Figure 5-2. This might include the Freundlich exponent which is one of the parameters that most influences pesticide losses in PESTRAS (Tiktak et al., 1994), but also parameters related to dispersion within soil or to the variation of pesticide degradation with depth. Also, default values for the calculation of derivatives and convergence and termination criteria supplied in PEST may be inadequate for this particular dataset, resulting in failure of the inverse modelling package to achieve convergence.

Although the model was calibrated against integrated concentrations over time, the calibration also resulted in an improvement of predictions for leaching patterns, maximum concentrations and cumulative loads for most of the lysimeters (Table 5-3). However, the better fit of model predictions to experimental data can be attributed, to some extent, to the use of lysimeter specific sorption and degradation parameters instead of median model parameters.

DISCUSSION

Only Kom and DT50 were allowed to vary in this inverse modelling exercise. These two parameters were found to be the most influential variables on predictions of pesticide loss for PESTRAS (Tiktak *et al.*, 1994) and PESTLA (Dubus *et al.*, 2002a), a model very similar to PESTRAS. The choice of parameters to be modified by the parameter estimation package is important as this is likely to greatly affect model predictions. The modeller needs to know which parameters most influence the output he/she is interested in matching. It may therefore be desirable to conduct a limited one-at-a-time sensitivity analysis of the model (analysis of the response of

the model to variations in an input, all other inputs being kept constant) unless the user is very familiar with the model. Failure to include the most influential parameters would mean that a parameter may have to be greatly varied to achieve a response similar to that obtained with a small variation in one of the more sensitive parameters. The exclusion of influential and uncertain parameters from the calibration may lead to the derivation of lumped, relative values for calibrated parameters. However, it is important to realise that a sensitivity analysis does not address the question of whether the parameters of interest can be determined independently and with sufficient accuracy (Finsterle & Faybishenko, 1999). Although an improvement in the goodness of fit of the simulations is desirable, it should not be achieved to the detriment of the quality of modelling.

Universal inverse modelling packages such as PEST (Doherty, 2000) or UCODE (Poeter & Hill, 1998) can be linked to almost any model provided it uses and produces ASCII files and can be run in batch mode. The large majority of pesticide leaching models meet these criteria. The application of inverse modelling methods to pesticide fate models is expected to have numerous advantages. Three specific uses can be anticipated. First, inverse modelling provides a means to automatically calibrate models to experimental data and is therefore a welcome alternative to time-consuming and subjective trial-and-error methods that are currently used in the calibration of water and pesticide components of pesticide leaching models. Although the tuning of some parameters manually until the model matches the data in some -often vague and subjective- sense can be rather successful in applications where the number of parameters is small, it suffers from a lack of exactness, reproducibility and objectivity (Janssen & Heuberger, 1995). Secondly, inverse modelling techniques could help determine adequate values for the most uncertain input parameters that cannot be determined routinely through experimentation. The third use, investigated here, envisages that inverse modelling may be used to derive sorption and degradation parameters which are specific to the field.

Sorption and degradation values derived by an inverse modelling approach might help to identify instances in which the use of laboratory values in modelling fails to

describe field behaviour and to derive alternative values in those circumstances. Laboratory half-lives are traditionally determined under conditions which differ markedly from those in the field. Reasons for discrepancy include the use of sieved, disturbed soil and the application of constant moisture and temperature conditions in laboratory experiments (Beulke *et al.*, 2000). The technique would also prove useful in cases where degradation data specific to the field/lysimeter have not been determined. Inverse modelling provides a degradation rate constant which is corrected for influences of fluctuations in temperature and moisture and can be tied to reference conditions. In contrast to field rates of dissipation, this parameter can thus be used for simulations under different climatic conditions. In conjunction with each of these uses, inverse modelling methods provide valuable information on the behaviour of the model, such as its sensitivity to changes in selected input parameters, its capability to describe observed data, and the correlation between calibrated parameters.

The present paper demonstrated the combination of PEST with the pesticide leaching model PESTRAS. Results indicate that inverse modelling has potential applications within pesticide fate modelling as described above. However, a number of issues are raised with respect to the robustness of the derivation of Kom and DT50 values by inverse modelling. A companion paper (Dubus *et al.*, 2002b) investigates i) the non-uniqueness associated with the calibrations of three of the seven lysimeters used in this study and ii) the influence of values attributed to the Freundlich exponent, a key parameter not included in the parameter estimation. These investigations are designed to assess the confidence that should be attributed to sorption and degradation values derived by inverse modelling.

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Table 5-1. Selected characteristics of the seven lysimeter studies

Lysimeter no.	Location [Ψ]	Soil name	Cropping [ΨΨ]	Duration	Total water input [§]	Sampling points
				years	mm	
1	A	Borstel	SW-WB-WR	2	1620	15
2	A	Schifferstadt	WW-WB-WR	2	1640	13
3	A	Schifferstadt	WW-WB-WR-WO	3	2414	19
4	B	Borstel	WW-WB-WR	2	1994	23
5	B	Borstel	WW-WB-WR	3	3123	35
6	B	Landau	P-WW-WW	3	2813	42
7	B	Landau	P-WW-WW	3	2813	42

[Ψ] A: Limburgerhof; B: Schmallenberg.
[ΨΨ] SW: Spring wheat; WB: Winter barley; WR: Winter rye; WW: Winter wheat; WO: Winter oilseed rape; P: Peas.
[§] Rainfall + irrigation

Table 5-2. Sorption and degradation data

	Sorption		Degradation	
	Kom	nf	Laboratory half-life	Field DT50
	mL g^{-1}		days	
Number of studies	11	11	21	10
Minimum	3.7	0.561	7.1	3.0
Maximum	101.9	1.125	86.6	21.0
Mean	26.1	0.839	25.9	12.9
Median	16.4	0.800	17.8	12.5

Table 5-3. Maximum herbicide concentrations in leachate and cumulative loads predicted by PESTRAS before and after automatic calibration by inverse modelling

Lysimeter no.	Maximum concentrations			Cumulative load		
	μg L^{-1}			mg m^{-2}		
	Observed[a]	Simulated prior to calibration	Simulated after calibration	Observed	Simulated prior to calibration	Simulated after calibration
1	0.027	0.030	0.018	0.005	0.005	0.004
2	0.128	0.050	0.108	0.016	0.014	0.018
3	0.178	0.114	0.124	0.043	0.037	0.040
4	0.060	0.214	0.053	0.029	0.080	0.017
5	0.060	0.221	0.042	0.046	0.105	0.039
6	0.084	1.480	0.038	0.038	0.667	0.015
7	0.065	0.236	0.021	0.014	0.072	0.003

[a] Maximum concentration in any single leaching event; annual average concentrations were <0.1 μg L^{-1}

Table 5-4. Initial and calibrated values for Kom and DT50

Lysimeter no.	Kom		DT50		Sum of squared residuals		Number of runs[ΨΨ]	Correlation[§]
	Initial	Calibrated[Ψ]	Initial	Calibrated[Ψ]	Before cal.	After cal.		
	mL g^{-1}		days					
1	16.4	9.8 (7.2-12.0)	17.8	11.0 (8.9-13.2)	1.73×10^{-3}	7.80×10^{-4}	64	0.988
2	16.4	8.2 (3.4-13.0)	17.8	11.9 (7.8-16.0)	2.94×10^{-2}	6.75×10^{-3}	32	0.967
3	16.4	15.7 (8.4-23.0)	17.8	17.4 (11.2-23.5)	6.74×10^{-2}	6.58×10^{-2}	18	0.981
4	16.4	21.0 (19.9-22.1)	17.8	17.7 (16.9-18.6)	1.60×10^{-1}	9.27×10^{-3}	27	0.963
5	16.4	37.9 (36.9-39.0)	17.8	32.4 (31.6-33.2)	2.04×10^{-1}	1.14×10^{-2}	47	0.971
6	16.4	32.2 (32.1-32.3)	17.8	21.7 (21.7-21.7)	1.83×10^{1}	4.44×10^{-2}	44	0.328
7	16.4	21.7 (20.8-22.6)	17.8	17.7 (16.8-18.6)	2.79×10^{-1}	1.44×10^{-2}	23	0.976

[Ψ] 95% confidence limits of calibrated parameters in parentheses.
[ΨΨ] Number of PESTRAS runs to achieve convergence .
[§] Correlation coefficients between Kom and DT50.

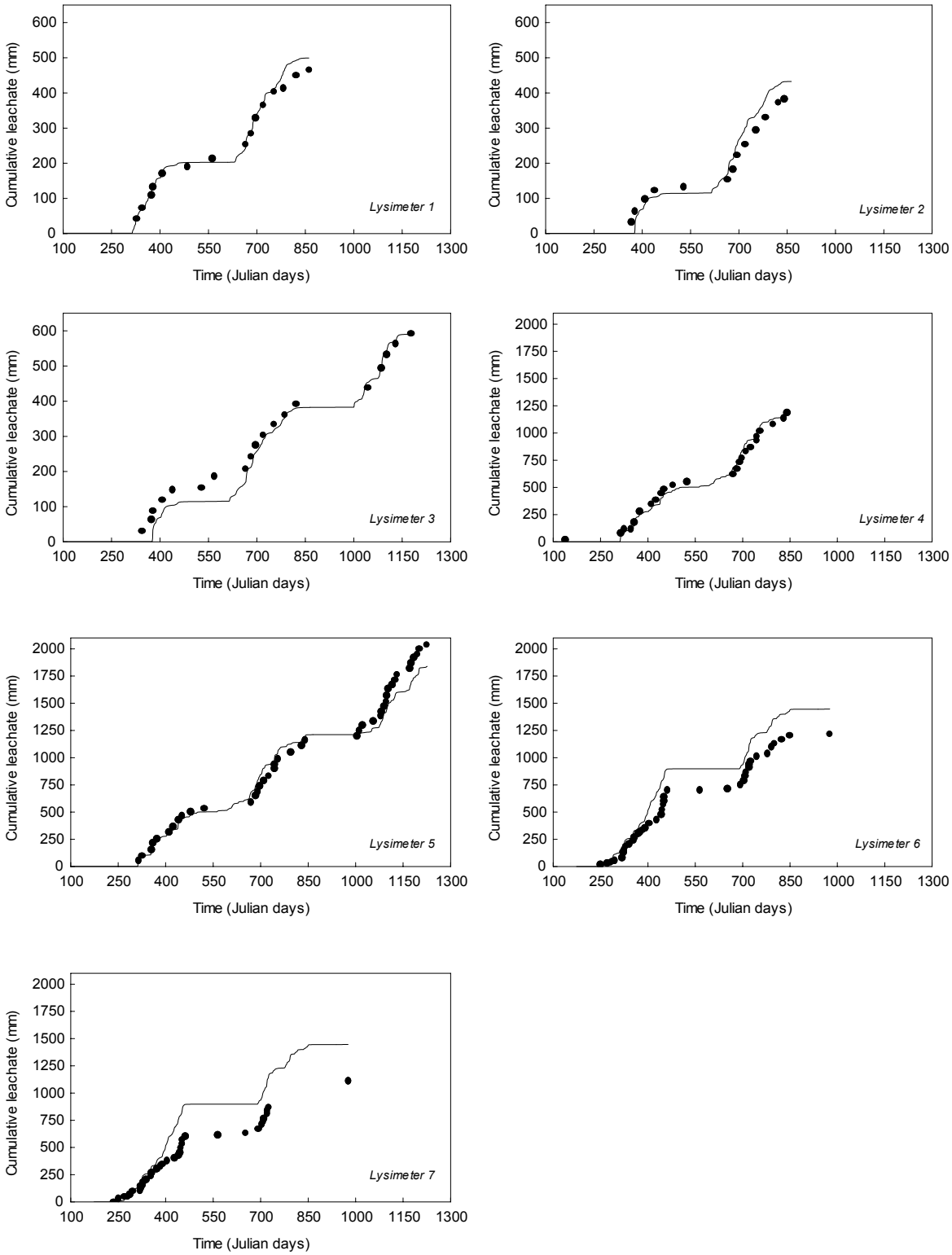

Figure 5-1. Comparison between observed cumulative volumes of leachate and those predicted by PESTRAS after a trial-and-error calibration. Black dots indicate observed data and the solid lines represent PESTRAS predictions. Day 1 is 1 January.

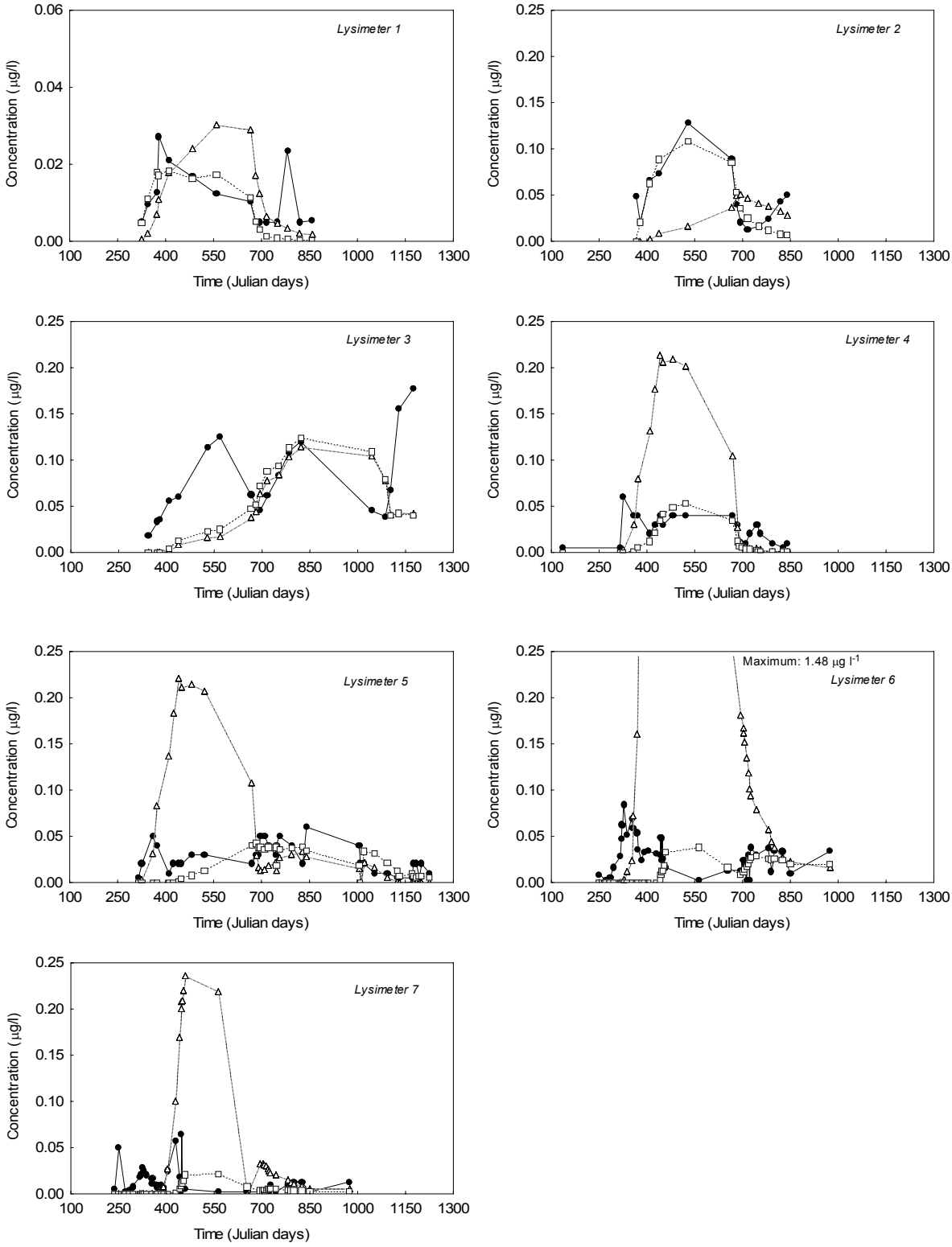

Figure 5-2. Comparison between observed herbicide concentrations in leachate (black circles), those predicted by PESTRAS using median DT50 and Kom values (open triangles) and those predicted by PESTRAS after calibration by inverse modelling (open squares). Day 1 is 1 January.

Chapter 6

INVERSE MODELLING FOR ESTIMATING SORPTION AND DEGRADATION PARAMETERS FOR PESTICIDES. PART 2: CALIBRATION NON-UNIQUENESS

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ABSTRACT

The leaching model PESTRAS was previously used to estimate sorption and degradation values for a herbicide from seven lysimeter datasets using an inverse modelling approach. The present paper reports on additional work with three of the lysimeter datasets to assess the influence on calibration results of i) values attributed to uncertain parameters not included in the calibration, and ii) starting values supplied to the inverse modelling package. In both instances, a strong effect on optimised Kom and DT50 values was observed. Automatic calibrations with different values for the Freundlich exponent nf yielded different combinations of Kom and DT50. Similarly, the supply of different starting values for Kom and DT50 revealed that different combinations of these two parameters equally calibrated PESTRAS for two of the three lysimeters. Overall, inverse modelling was found to be a flexible and powerful investigative tool for the calibration of pesticide leaching models and for the estimation of sorption and degradation parameters from field data. Still, non-uniqueness issues were encountered and the derivation of values for sorption and degradation (or any other) parameters through inverse modelling may

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result in lumped estimates integrating inaccuracies, uncertainties and limitations associated with experimental data, modelling and calibration. The technique should be used with care and the reliability in calibration results and parameter values obtained through inverse modelling should be considered a priority in any exercise. Lattice modelling, *i.e.* the running of the model for different combinations of Kom and DT50 values varied by a constant increment and calculation of the goodness-of-fit to the experimental data, was found to be useful for identifying those instances where non-uniqueness is expected.

INTRODUCTION

In the first paper of this two-part series, Dubus and co-workers reported on the derivation of sorption and degradation values from seven lysimeter datasets using an inverse modelling approach and the pesticide leaching model PESTRAS (Dubus *et al.*, 2002a). Results indicated that inverse modelling has potential applications in the field of pesticide fate simulation to improve model performance, to back-calculate key model inputs and to generate valuable information on the behaviour of the models. Specifically, the technique may help to identify instances where the use of pesticide sorption and degradation parameters measured in the laboratory fails to describe field behaviour and to derive alternative values direct from the field data. However, the first paper also raised a number of issues related to the robustness of the inverse modelling approach when applied to pesticide leaching models. The present paper reports additional work with three of the seven lysimeter datasets to assess the confidence that should be attributed to sorption and degradation values derived by inverse modelling.

A critical component of inverse modelling is the selection of appropriate parameters to include in the calibration (Dubus *et al.*, 2002b). Dubus *et al.* (2002a) chose to calibrate Kom (the sorption distribution coefficient normalised to organic matter Kom) and DT50 (the time required for 50% degradation of the pesticide in an incubation experiment as determined using first-order kinetics) as both are largely

uncertain and have a strong influence on model predictions for pesticide losses (Tiktak *et al.*, 1994; Dubus *et al.*, 2002c). All other parameters were held constant throughout the calibration. In the present paper, we investigate the influence on calibration results of values attributed to a third influential parameter not varied during the calibration. The Freundlich exponent nf was selected for this purpose as it has a significant influence on the predictions for pesticide loss by PESTRAS (Tiktak *et al.*, 1994) and other pesticide leaching models (Boesten, 1991; Dubus & Brown, 2002; Dubus *et al.*, 2002c). As for Kom and DT50 values, nf is subject to uncertainty due to the inherent variability in environmental and experimental conditions and user-subjectivity in the selection of an adequate value from the range of those available. Initial calibrations with the seven lysimeter datasets were carried out with the Freundlich exponent nf set to the median from 11 sorption studies (Dubus *et al.*, 2002a). Here, automatic calibrations were undertaken for three of the lysimeter datasets using a range of values for nf.

Results reported by Dubus *et al.* (2002a) also suggested that Kom and DT50 were correlated to some extent within the calibration. Parameter correlation is common in environmental modelling although it is often overlooked when manual approaches to calibration are used (Poeter & Hill, 1997). Large correlation between optimised parameters is likely to result in non-uniqueness of calibration results. Non-uniqueness, non-identifiability and instability can all contribute to the ill-defined nature of inverse problems (Weiss & Smith, 1998) and may result in meaningless solutions (Carrera & Neuman, 1986). To investigate the influence of parameter correlation on results from inverse modelling, a large number of automated calibrations were carried out with a range of starting values for Kom and DT50. Output from this exercise was used to devise and test a partial solution to parameter correlation. The method is designed to identify the presence and location in the parameter space of any global minimum in the lack-of-fit statistic.

MATERIALS AND METHODS

Selection of datasets

Three datasets (#1, #3 and #6) were selected from the seven lysimeter datasets used in the first paper to represent a range of situations with regard to inverse modelling results. Lysimeter #1 saw a significant improvement in the fit of pesticide concentrations in leachate after Kom and DT50 were calibrated using PEST. In contrast, the simulation of pesticide breakthrough for lysimeter #3 did not benefit substantially from the automated fitting of the two parameters. The sixth dataset was taken as representative of situations where a large number of datapoints are available and where an improvement in the fit was obtained by inverse modelling although there remained significant discrepancy between simulated and experimental data.

Influence of nf values of calibration results

Initial estimates of Kom and nf values used in the original calibration exercises (Kom 16.4 ml/g; nf 0.8) were taken as the median of 11 values obtained in batch equilibrium sorption experiments. Here, the influence of the nf value on calibration results was investigated to address the uncertainty in the attribution of a value to this parameter. Calibrations similar to those described in the first of this two-part series (*i.e.* calibration of PESTRAS against lysimeter data by modifying Kom and DT50) were conducted for different nf values. These were varied between 0.56 and 1.12 (the minimum and maximum values reported in laboratory experiments) using a 0.01-unit increment. This resulted in 57 calibration exercises for each of the three lysimeters. At the end of each calibration, calibrated values, correlation between Kom and DT50, the number of runs to achieve convergence, eigenvalues and the value for the objective function were stored for later analysis.

Influence of starting values on calibration results

In the initial calibrations (Dubus *et al.*, 2002a), a single combination of starting values were used in the initial calibrations for the seven lysimeters (Kom 16.4 ml/g; DT50 17.8 days). Here, the influence on calibration results of starting values provided to the PEST package (Doherty, 2000) were investigated for the three datasets selected. Combinations of starting values for Kom and DT50 were obtained by varying Kom between 2 and 30 ml/g and DT50 between 2 and 30 days using an increment of 2 units for each parameter and by combining all possible Kom and DT50 values. This resulted in a total of 225 calibration exercises for each of the three datasets. For each calibration performed, the following information was extracted from the PEST record file: values for Kom and DT50 at the end of the calibration, number of model runs carried out, reason for ending the calibration, value of the Φ statistics and correlation between Kom and DT50 within the calibration.

Forward modelling on a grid

The PESTRAS model was run in a forward manner (as opposed to the inverse modelling approach) for multiple combinations of Kom and DT50 values. Parameter values were varied between 2 and 30 ml/g (40 ml/g for lysimeter #6) and between 2 and 30 days (40 days for lysimeter #6) for Kom and DT50, respectively. An increment of one unit was applied to both parameters and this resulted in a total of 841 combinations (1521 combinations for lysimeter #6) of Kom and DT50. A model run was performed for each of these combinations and the sum of squared residuals (Φ statistics) which is used by PEST for assessing the lack-of-fit was calculated for each run:

$$\Phi = \sum_{i=1}^{n} \omega_i^{\,2} \times \left(O_i - P_i\right)^2$$

where O_i is the ith observed concentration;

P_i is the model prediction for the ith concentration;

ω_i is the weight attributed to the *i*th observation (here ω_i=1 for all observations);
n is the number of observations.

The lack- (Φ) and goodness- (Φ^{-1}) of-fit was analysed using a three dimensional representation against Kom and DT50 values. As noted by Hopmans and Šimunek (1999), response surface analysis is helpful in revealing the occurrence of local minima, the presence of a well-defined global minimum, parameter sensitivity and correlation.

RESULTS

Influence of nf values on calibration results

Investigation of the influence of nf value on calibration results for the three lysimeters resulted in a total of 6,860 PESTRAS runs. The number of model runs required to end calibration ranged between 7 and 98. The latter number was obtained for a nf value of 1.06 for lysimeter #6. Scenarios where only seven model runs were necessary to end calibration reflected the lack of sensitivity of the goodness-of-fit function to variations in Kom and DT50 applied by PEST. This occurred for all three lysimeters for small values of nf (*i.e.* nf < 0.67). Figures 6-1 to 6-3 present calibration results for different nf values for lysimeters #1, #3 and #6, respectively (only those final calibrated values which differed from the starting values supplied to PEST are shown). For all lysimeter datasets, the use of different nf values resulted in different combinations of calibrated Kom and DT50 values thereby reflecting the significant sensitivity of PESTRAS to the Freundlich exponent (Tiktak *et al.*, 1994).

For lysimeter #1 (Figure 6-1), the use of different nf values resulted in larger DT50 values being compensated by smaller Kom values in the calibration (Pearson r 0.78, $p<0.01$). An increase in nf value resulted in a decrease in DT50 ($p<0.01$) and an

increase in Kom ($p<0.01$). The variation of calibrated Kom values against nf followed a clear exponential relationship ($r^2=1.00$, $p<0.01$), reflecting the mathematics of the Freundlich equation which is used to describe pesticide sorption in PESTRAS (equation 2 in Dubus *et al.*, 2002a). All combinations of Kom and DT50 presented in Figure 6-1 successfully calibrated the PESTRAS model for the different nf values used. A decrease in the Φ function which represents the lack-of-fit between the model and the lysimeter data was obtained by lowering the nf value and calibrating the model against Kom and DT50. Below a nf value of 0.78, PEST returned the starting values supplied, which reflects the inability of the package to calibrate the model for small values of this parameter. The relative change in the Φ function for the calibrations was small (maximum variation 4.0%) although the variation of nf applied was significant. This stability was reflected in the pesticide breakthrough curves being similar for the different combinations of calibrated Kom and DT50 (Figure 6-4).

Results for lysimeter #3 (Figure 6-2) contrasted with those obtained for lysimeter #1 in that: i) the correlation between calibrated Kom and DT50 values for the different nf values was positive (Pearson r 0.79, $p<0.01$); ii) the use of larger Freundlich values resulted in larger calibrated DT50 values (Pearson r 0.66, $p=0.06$); and iii) smaller values of the Φ function (*i.e.* improved fit to the simulated data) were obtained when larger nf values were used. As for lysimeter #1, an exponential relationship between calibrated Kom and nf values was found although deviations from the curve were more frequent and larger than for the first dataset. These deviations may reflect the difficulty encountered by PEST in finding the minima of the Φ function for a number of modelling scenarios corresponding to specific values of nf. Pesticide breakthrough curves obtained using the calibrated parameter values were more scattered than those for lysimeter #1 (Figure 6-4) although the overall shape remained similar for all calibrations.

Results for lysimeter #6 provided a third behaviour with respect to the influence of nf values on calibrated values for Kom and DT50. For nf values <0.82 and >0.87, calibrated DT50 values were relatively constant when nf was varied. Calibrated

values were 21.2-22.3 days and 6.3-6.4 days for nf<0.82 and nf>0.87, respectively. The grouping was also reflected in calibrated values for Kom which were distributed along two exponential curves when plotted against nf. The chart plotting the Φ function against nf showed that two types of Φ values were obtained depending on the value of nf. These differences were reflected in different calibrated pesticide breakthrough curves (Figure 6-4). In some instances, the calibration of PESTRAS resulted in the model not simulating the first increase in concentrations (day 271 to day 461) and over-estimating measured concentrations from day 450 to day 562. The magnitude of concentrations from day 694 was somewhat better simulated although the model failed to simulate the low concentrations in leachate collected on day 792 and 850. The associated Φ values were ca. 1.8×10^{-2}. Pesticide breakthrough curves which corresponded to smaller Φ values were those which provided a good fit to the initial increase in concentrations in leachate, but then failed to simulate the presence of the compound in leachate from day 450 onwards (Figure 6-4). A range of intermediate curves between the two broad groupings described above were obtained in a small number of cases. Occasionally, an increase in nf value by 1 unit (*e.g.* from nf 0.94 to nf 0.95 or from nf 0.95 to nf 0.96) resulted in calibrated Kom and DT50 values providing very different pesticide breakthrough curves.

The use of different values for nf resulted in the derivation of different calibrated values for Kom and DT50 for all three lysimeters. Different types of behaviour with regard to calibration were identified for the three lysimeter datasets used. In some instances (*e.g.* lysimeter #1), Kom and DT50 compensated for each other and different calibrated Kom-DT50 combinations resulted in similar predictions of pesticide breakthrough. In contrast, lysimeter #6 demonstrated that variations in nf values may result in calibrated Kom-DT50 combinations which lead to different pesticide breakthrough curves. The selection of a range of adequate values for nf for lysimeter #6 may be based on a visual assessment of pesticide breakthrough curves although this process is likely to be subjective. Selecting a value for nf on the basis of the calibration results for lysimeter #1 is made difficult by the derivation of similar pesticide breakthrough curves for different nf values. The examination of the variation of the overall goodness-of-fit provided little help for the selection of a nf

value (and hence a Kom-DT50 combination) since the Φ function increased monotonously with increasing nf (a monotonous decrease was found for lysimeter #6). Such a selection would have been possible if the Φ function had shown a clear minimum within the range of nf values covered here.

Influence of starting values on calibration results

A total of 225 combinations of Kom and DT50 starting values were supplied to PEST for each lysimeter dataset and this resulted in a total of 27,159 PESTRAS runs. Calibrated Kom and DT50 values are presented in Figure 6-5 and resulting pesticide breakthrough curves simulated by the model are shown in Figure 6-6. The grid nodes in Figure 6-5 correspond to the 225 initial combinations of starting values supplied to PEST.

Calibration results were found to be dependent on starting values for lysimeter #1. For combinations of Kom and DT50 starting values falling below the 1:1 line, most calibrations were unsuccessful and starting values were returned by PEST at the end of the calibration. However, two convergence zones were identified. The first zone corresponds to very small Kom values with DT50 values in the range 1.3-4.4 days. Most of the Kom values were at the lower bound of variation which was supplied to PEST (10^{-10}). These Kom values are clearly not reasonable. The second convergence zone was fairly small in the parameter space and was defined by the following values for Kom and DT50: $9.6<Kom<10.7$ and $10.8<DT50<12$. Only five combinations of calibrated values did not fall into any of these three categories. Combinations of starting values were classified on the basis of the calibration results (Figure 6-7). The figure shows that calibration results were likely to fall into the first convergence zone if starting values were below the 1:1 line while combinations of starting values situated above the 1:1 line resulted in calibrated values in the second convergence zone. Calibrations in the second convergence zone provided very similar pesticide breakthrough curves (Figure 6-6). Curves which gave little resemblance with the experimental data in Figure 6-6 were those corresponding to the first convergence zone with small Kom values.

Four types of calibration behaviour were identified for lysimeter #3 on the basis of the position of the combination of starting values in the parameter space. For starting combinations falling below a regression line between Kom and DT50 (Figure 6-5), PEST either returned starting values or very small values for Kom and DT50 (Figure 6-6) or failed to provide calibration results because the gradient of the Φ function became zero. As for lysimeter #1, calibration was only successful for combinations of starting values above a particular line (Figure 6-7), but in this instance, calibrated values for Kom and DT50 fell onto a curve (Figure 6-5) rather than being concentrated in a convergence zone. Pesticide breakthrough curves corresponding to these calibrated values varied significantly (Figure 6-6) although numerically, the 117 calibrations falling on this line provided a very similar fit to the data (Φ values 0.060 to 0.069; data not shown).

Lysimeter #6 showed a complex behaviour when compared to the other two datasets. Again, depending on the combination of starting values (Figure 6-5), the following results could be obtained: failure to calibrate because of an insensitivity of the Φ function to Kom and DT50; the return of starting values; a first convergence zone with small values of Kom; a second convergence zone regrouping 63 calibrations defined by 5.8<Kom<6.2 and 6.3<DT50<6.5; a third convergence zone regrouping 89 calibrations defined by 32.1<Kom<33.1 and 21.6<DT50<22.4; and, a convergence curve that was less well defined than for lysimeter #3. Calibrations which provided a good fit to the first peak in pesticide breakthrough were related to the second convergence zone. Calibrations belonging to the third zone yielded pesticide breakthrough curves which were closer to the data from day 650 onwards (Figure 6-6). The final values of the Φ function were 0.180 and 0.048 for the second and third convergence zones, respectively.

Lattice modelling

Forward modelling for multiple combinations of Kom and DT50 was undertaken to try to understand the difference in calibration behaviour shown by the three lysimeter datasets in relation to the use of different starting values for Kom and DT50. For lysimeter #1 and #3, values of Kom and DT50 were modified between 2 and 30 ml/g, and between 2 and 30 days, respectively, using a one-unit increment step for both parameters. Ranges of variation were 2-40 ml/g and 2-40 days for lysimeter #6 because earlier investigations related to starting values had suggested a convergence zone for values of Kom>30 ml/g and DT50 >30 days (data not shown). The sum of squared residuals between the simulated and measured concentration data (the Φ statistics) was calculated for each run. The approach is referred to as "lattice modelling" because of the visual aspect of the results obtained. Figure 6-8 presents surface and contour plots of the variation of the reciprocal of the Φ statistics for all combinations of Kom and DT50 for all three lysimeters. Depicting Φ^{-1} provided clearer 3D representations of error surfaces and ultimately more information than the plotting of Φ (figure not shown). In the plots, the best fit to the experimental data is obtained for the smallest values of Φ (a lack-of-fit statistic) hence the largest values of Φ^{-1} (a goodness-of-fit statistic).

Figure 6-8 for lysimeter #1 shows that within the parameter space explored, the goodness-of-fit surface showed two flat regions divided by a ridge. The flat section for low Kom values (bottom left corner of Figure 6-8) corresponds to those combinations of Kom and DT50 which resulted in a large overestimation of pesticide concentrations in leachate while the other flat section (top right corner of Figure 6-8) corresponds to those values of Kom and DT50 which resulted in negligible leaching predicted by PESTRAS. The Φ^{-1} function for these latter runs thus equalled the sum of the reciprocal of the squared measured concentrations (Φ^{-1}=371). The parameter space was divided by a ridge with steep slopes which reflect the large sensitivity of Φ^{-1} in this region of the parameter space. A peak clearly identifiable on the contour plot in Figure 6-8 was observed for approximately Kom 10 ml/g and DT50 11 days, which is consistent with the convergence zone observed for the calibration of

lysimeter #1 (Figure 6-5). No large increase in the Φ^{-1} statistics was observed for very low values of Kom, which confirms that convergence zone I in Figure 6-5 is an artefact created by PEST. This resulted from PEST assigning a value of 10^{-10} to calibrated Kom, the value which was supplied as the minimum bound of variation for Kom. PEST was unable to calibrate PESTRAS in those specific instances. When investigating the influence of starting values on calibration results, a number of calibrations resulted in PEST returning the starting values (Figure 6-5) since the package found that the "phi gradient [was] zero". This lack of sensitivity of Φ^{-1} corresponded to flat portions of the error surface in the top right sections of Figure 6-8.

Results of PESTRAS runs obtained for lysimeter #3 were similar to those for lysimeter #1 in that two flat sections were separated by a ridge. However, surface and contour plots suggest that there was no clear maximum on this crest. Instead, the contour plot suggests that very similar Φ^{-1} values could be obtained for a large number of combinations of Kom and DT50. These results are consistent with those obtained earlier where multiple combinations of calibrated values falling on a line were returned by PEST when different starting values were supplied (Figure 6-5).

In common with results for lysimeters #1 and #3, the Kom-DT50 parameter space was divided into two flat sections and a ridge for lysimeter #6 (Figure 6-8). There was a sharp increase in Φ^{-1} around Kom 6 ml/g and DT50 7 days corresponding to a clear convergence zone (Figure 6-5), but in contrast to lysimeter #1, the rest of the Φ^{-1} values situated on the ridge were similar (Figure 6-8). This can be best observed on the contour plot. These patterns are consistent with the existence of convergence zone II in Figures 6-5 and 6-7 and the presence of a convergence curve. As for the other two lysimeters, convergence zone I (Figures 6-5 and 6-7) appears to be an artefact reflecting the inability of PEST to calibrate PESTRAS for specific starting values. A local maximum of the Φ^{-1} function corresponding to the third convergence zone (*i.e.* 32<Kom<34 ml/g and 20<DT50<24 days) could be identified on the ridge although the 3D positioning of Figure 6-8 selected for presentation does not allow the identification of the small increase in the Φ^{-1} values.

DISCUSSION AND IMPLICATIONS

Investigations on the influence of the value attributed to the Freundlich exponent nf (a parameter not included in the initial calibrations) revealed that different calibrated Kom-DT50 combinations equally describing the experimental data could be obtained for different nf values. The Kom parameter compensated for changes in the values of nf. Calibration results could not be used to select an adequate value for nf from a range of possible values since the goodness-of-fit monotonously increased or decreased with increasing nf values. Adding nf to the list of parameters to be optimised is not a viable option since Kom and nf would compensate for one another within the calibration and this would lead to an ill-defined calibration problem. It is therefore suggested that, provided Kom, DT50 and nf are the most influential parameters on the prediction of pesticide concentrations: i) calibrations against pesticide leaching in lysimeter experiments are restricted to the parameters Kom and DT50; and, ii) a number of calibrations are carried out for different nf values. The latter point will help to assess the confidence that should be attributed to Kom and DT50 values derived by inverse modelling.

For the three lysimeters, the calibration behaviour for Kom and DT50 was dependent on the location of the Kom-DT50 starting values in the parameter space. Combinations of starting values falling below a line in a DT50 vs. Kom plot led to a failure to calibrate (*i.e.* return of starting values after a few runs or setting of Kom to the smallest value as specified in the possible variation range). A number of reasons can be put forward to explain the fact that PEST failed to find the convergence zones for these starting combinations. First, default values for derivative calculation and termination settings provided in PEST were used in the calibration. These default settings might be inadequate for the present inverse modelling problem and might need adjusting to achieve more consistent results. Secondly, the implementation of the Gauss-Levenberg-Marquardt in PEST might be inadequate for dealing with the present calibration problem where large portions of the error surfaces were found to show little sensitivity to changes in parameter values. The type of behaviour

revealed here by lattice modelling would provide a challenge to any algorithm for non-linear estimation and the performance of other inverse modelling packages, such as UCODE (Poeter & Hill, 1998), SUFI (Abbaspour *et al.*, 1997) or SUSE (Gottesbüren et al., 1996), therefore needs to be assessed. Thirdly, the computation of derivatives of all observations with respect to all adjustable parameters might not be accurate enough to permit a robust implementation of the Gauss-Levenberg-Marquardt procedure. The presence of round-off errors incurred in the calculation of derivatives is the most common cause of PEST failure to achieve a robust calibration (Doherty, 2000). Accuracy of the derivatives will be mainly dependent on the accuracy of the resolution of differential equations by PESTRAS and on the rounding of PESTRAS predictions in the model output. Inaccuracies resulting from these two sources will aggregate. PESTRAS has been developed for simulation purposes and is not optimised for inverse modelling applications. Dedicated model codes and procedures for parameter estimation may have to be developed to obtain reliable model derivatives and robust estimates of Koc and DT50 (Dieses *et al.*, 1999). For combinations of starting values other than those which returned starting values, calibration behaviour was dependent on the dataset considered. In some instances, starting combinations led to a more or less unique set of calibrated parameters, as in lysimeter #1. In other cases, calibration results were not unique and a range of Kom and DT50 values were returned. Again, the failure to return a unique combination of parameters might be attributed to an inadequate parameterisation of PESTRAS or PEST, the lack of precision in the calculation of derivatives, but also to the fact that the pesticide concentration data used might not enable the derivation of a unique Kom-DT50 combination. A parallel can be drawn with the field of soil water physics where inverse modelling is traditionally used to assess soil hydraulic properties from column experiments (Hopmans & Šimunek, 1999). The use of water outflow data only will lead to non-uniqueness issues in the calibration, but the integration of additional data (*e.g.* tensiometric measurements) will make the calibration problem better posed. Further research is required into the identification of the data requirements for a robust calibration of the water and pesticide components of leaching models. This might best be achieved through response surface analysis (Toorman *et al.*, 1992) and optimal experimental design which

enables the identification of data requirements for a well-posed calibration problem prior to conducting experiments. The presence of a large number of combinations of Kom and DT50 providing a similar goodness-of-fit to the data suggests that it may not be possible to derive robust Kom and DT50 values on the basis of leaching data from lysimeter experiments alone. In the present system, Kom and DT50 derived by inverse modelling are likely to have acted as fitting parameters. These parameters will have integrated inaccuracies and deficiencies in the structure of the model, its parameterisation and in the experimental data and will have lost part of their physical, chemical and biological definition (Dubus *et al.*, 2002b).

The examination of 3D-charts plotting Φ or Φ^{-1} against Kom and DT50 following forward modelling (referred to as lattice modelling) was useful in explaining the different calibration behaviours observed earlier. The plotting of the error surface as a stand-alone activity (*i.e.* without recurring to inverse modelling packages) could be of more general interest for identifying instances where there is no clear global minimum of the Φ function in the calibration of pesticide leaching models and hence where non-uniqueness in optimisation using inverse modelling packages is likely. Provided the grid extends over large ranges of Kom and DT50 values and the grid mesh is fine enough, this approach provides a way to easily identify whether a convergence zone exists and its location in the parameter space. The approach thus provides a practical solution to non-uniqueness issues where pesticide leaching models are used to estimate Kom and DT50 values. It was found to be effective in terms of running time when compared to the investigation of the influence on calibration results of using different starting values as presented earlier in this paper. The main limitations are that i) only two parameters can be considered for an easy visual assessment of the error surface in three dimensions; and ii) the technique should be restricted to those models with a short running time, *i.e.* a few seconds to a few minutes. Here, lattice modelling helped to characterise the correlation in the modelling between Kom and DT50, which resulted in calibration non-uniqueness. Poeter and Hill (1997) suggested two approaches for dealing with large correlation between parameters. The first is to set one of the parameters to a given value and estimate the other. This approach cannot be implemented in the present situation

since both Kom and DT50 are uncertain parameters and one would not have any confidence in assigning a particular value to either parameter. The second is to collect and include in the calibration additional data that will uniquely define all parameter values.

In comparison to the more traditional manual calibration, automated techniques for calibration are particularly useful for assessing the confidence that should be assigned to calibration results. However, the present investigations also demonstrated that inverse techniques should be used with care, particularly with respect to non-uniqueness. Sorption and degradation parameters derived by inverse modelling are theoretically better suited than field values to conduct extrapolations to other climatic conditions. However, average or median laboratory values will remain the primary input at lower tiers of regulatory modelling. Inverse modelling can help identify instances in which laboratory values fail to describe the field behaviour and provide alternative values in those instances. These values should be regarded as additional information helping to build an overall picture of how a crop protection product is likely to behave once released into the environment.

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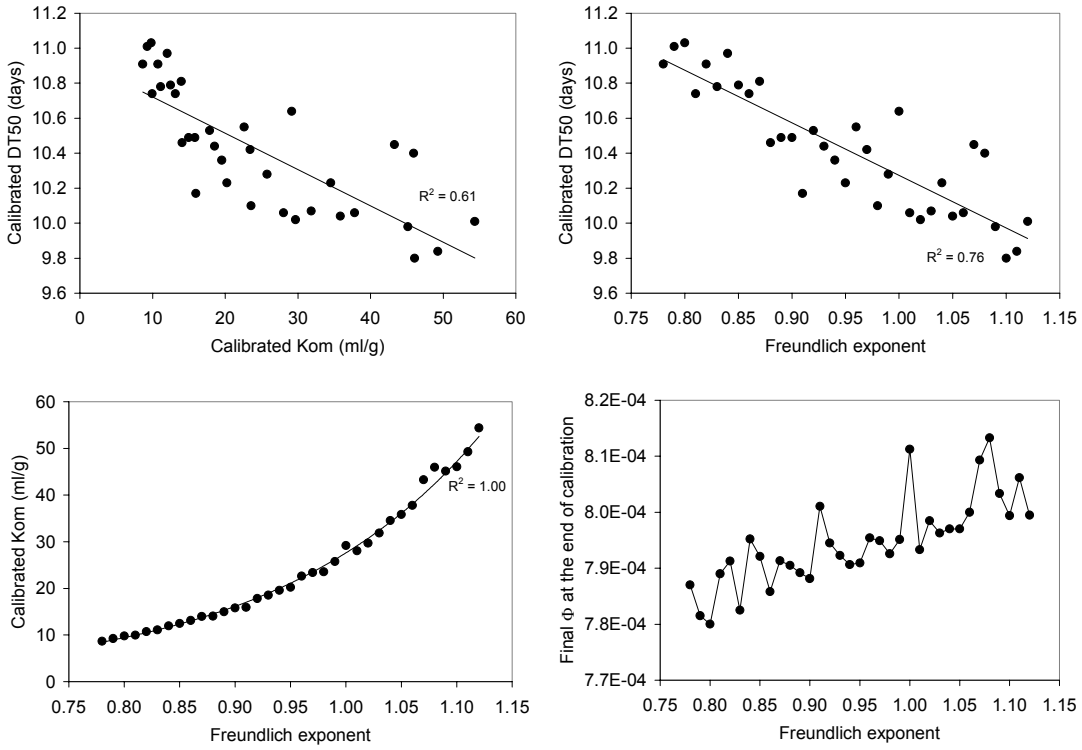

Figure 6-1. Calibration results for different values of nf for lysimeter #1.

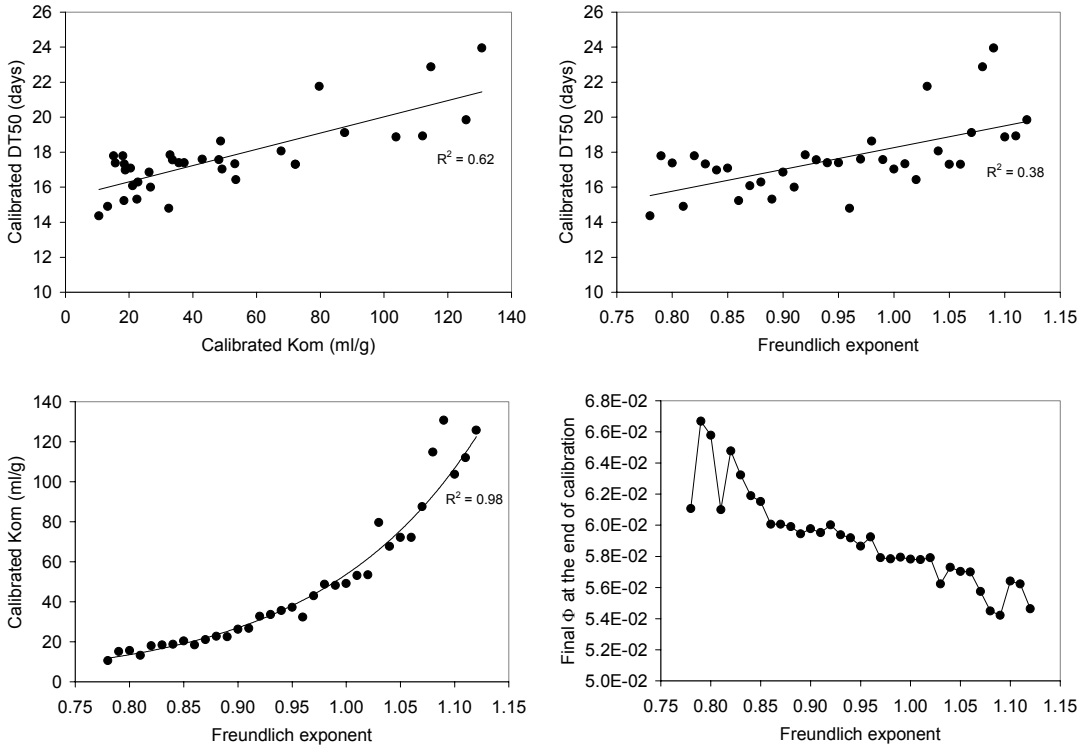

Figure 6-2. Calibration results for different values of nf for lysimeter #3

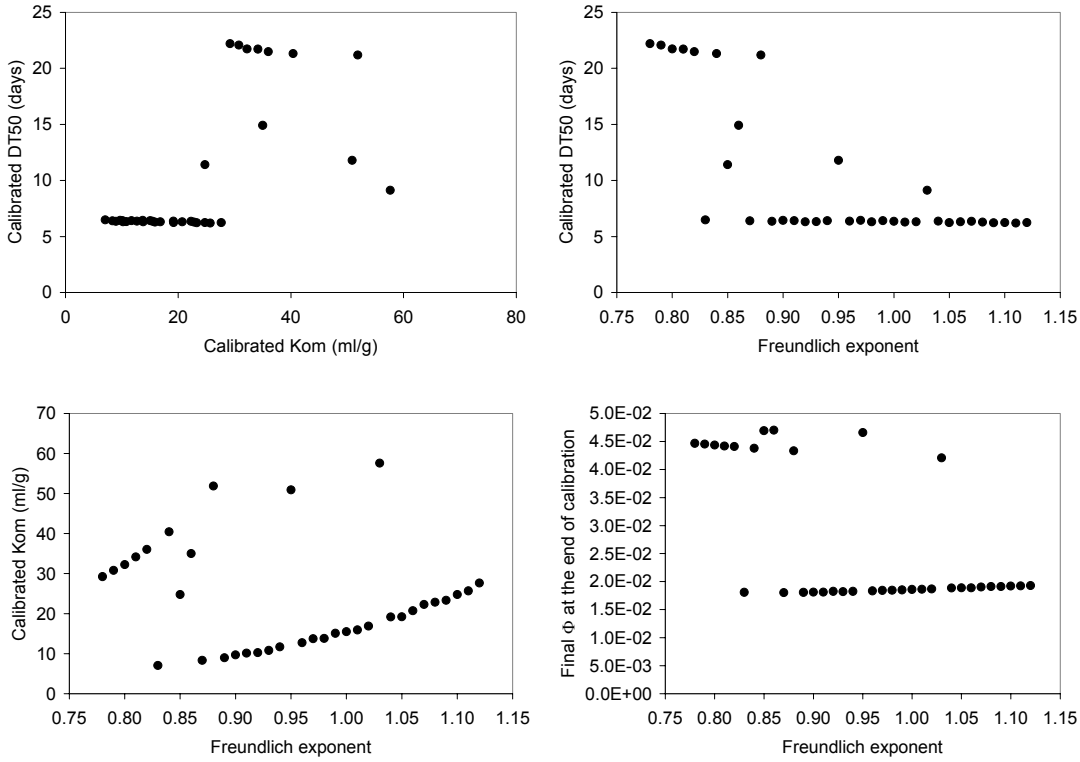

Figure 6-3. Calibration results for different values of nf for lysimeter #6

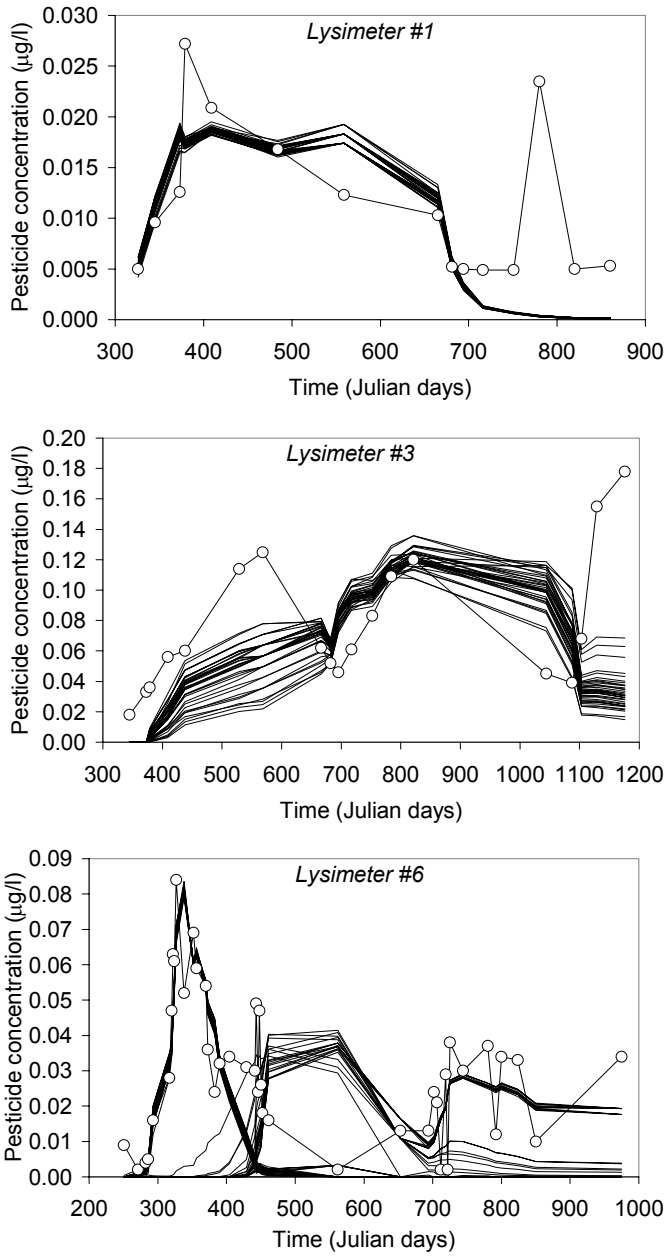

Figure 6-4. Pesticide breakthrough simulated after calibration of PESTRAS for different nf values (plain lines). The experimental data are shown by open circles.

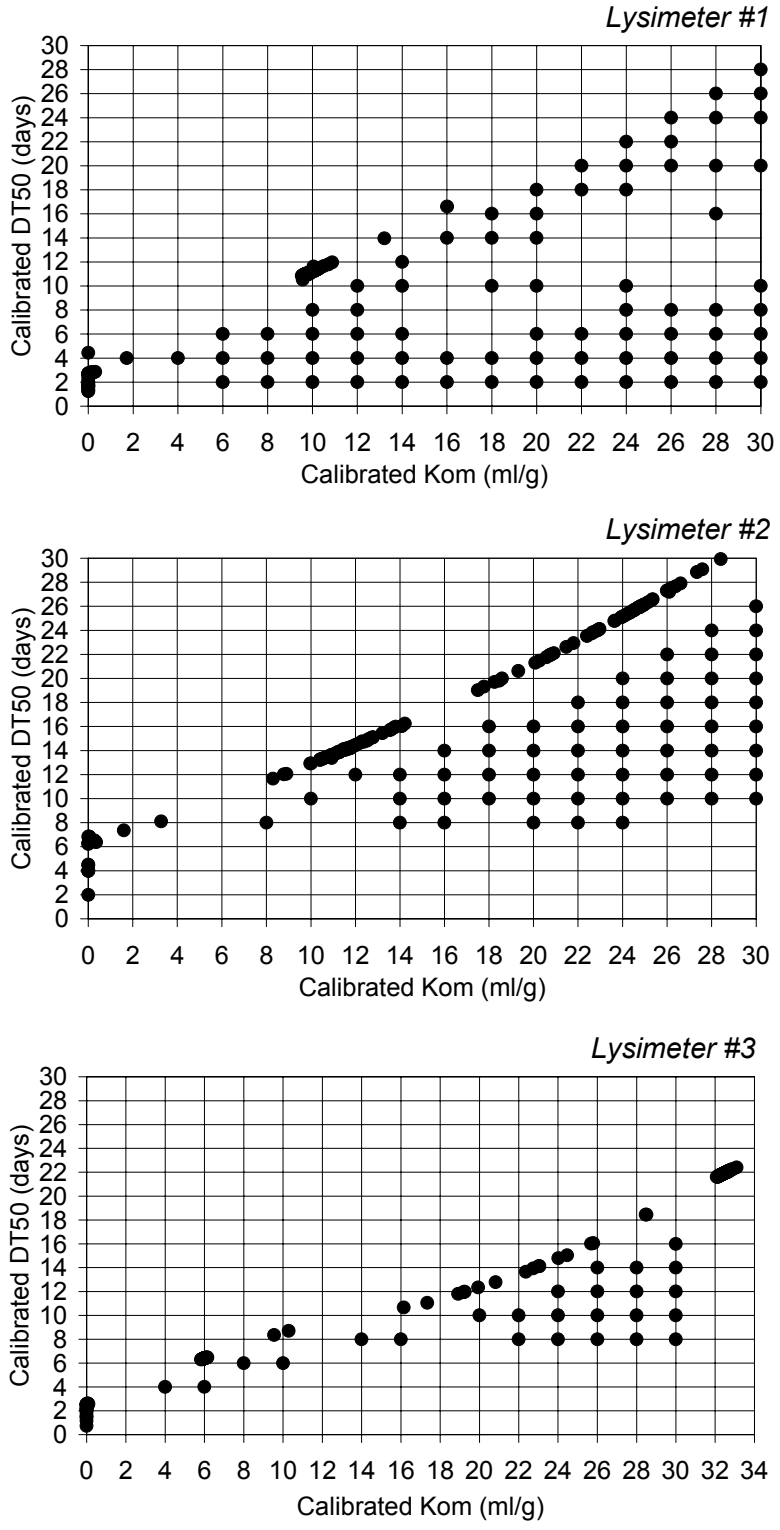

Figure 6-5. Combinations of calibrated Kom and DT50 values obtained for different starting values. Calibrated values are represented by closed circles. Starting values are represented by grid nodes.

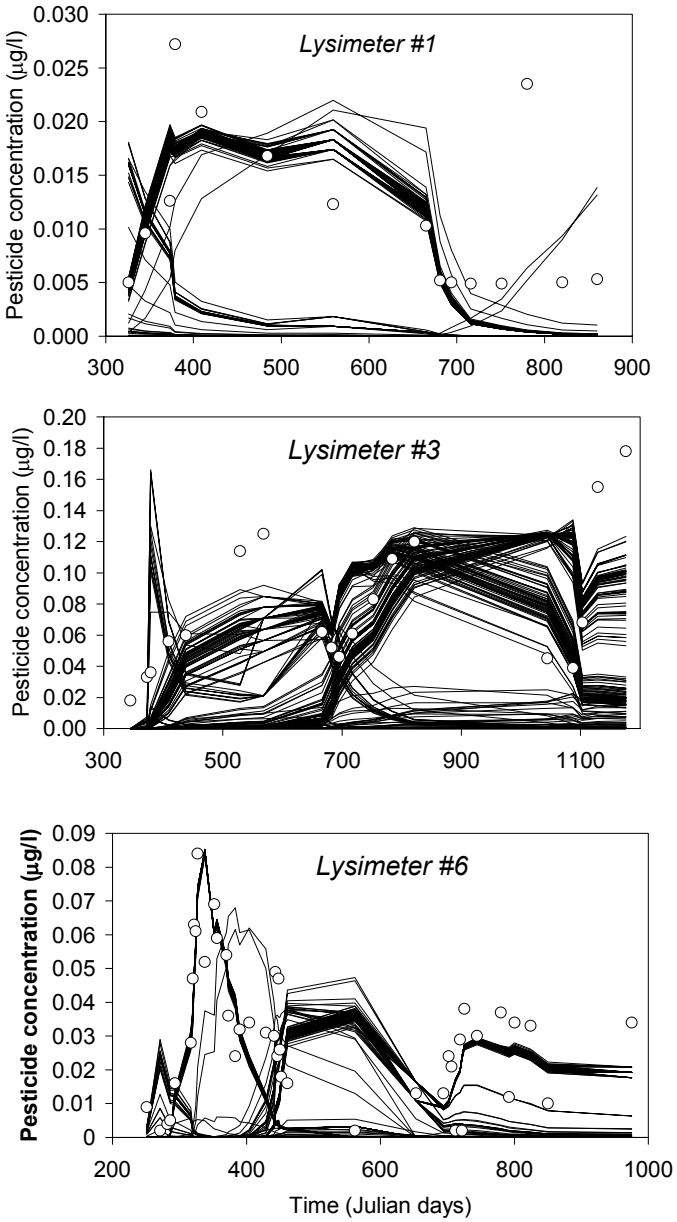

Figure 6-6. Populations of pesticide breakthrough curves obtained for calibrations carried out with different starting values. The measured data are represented by open circles.

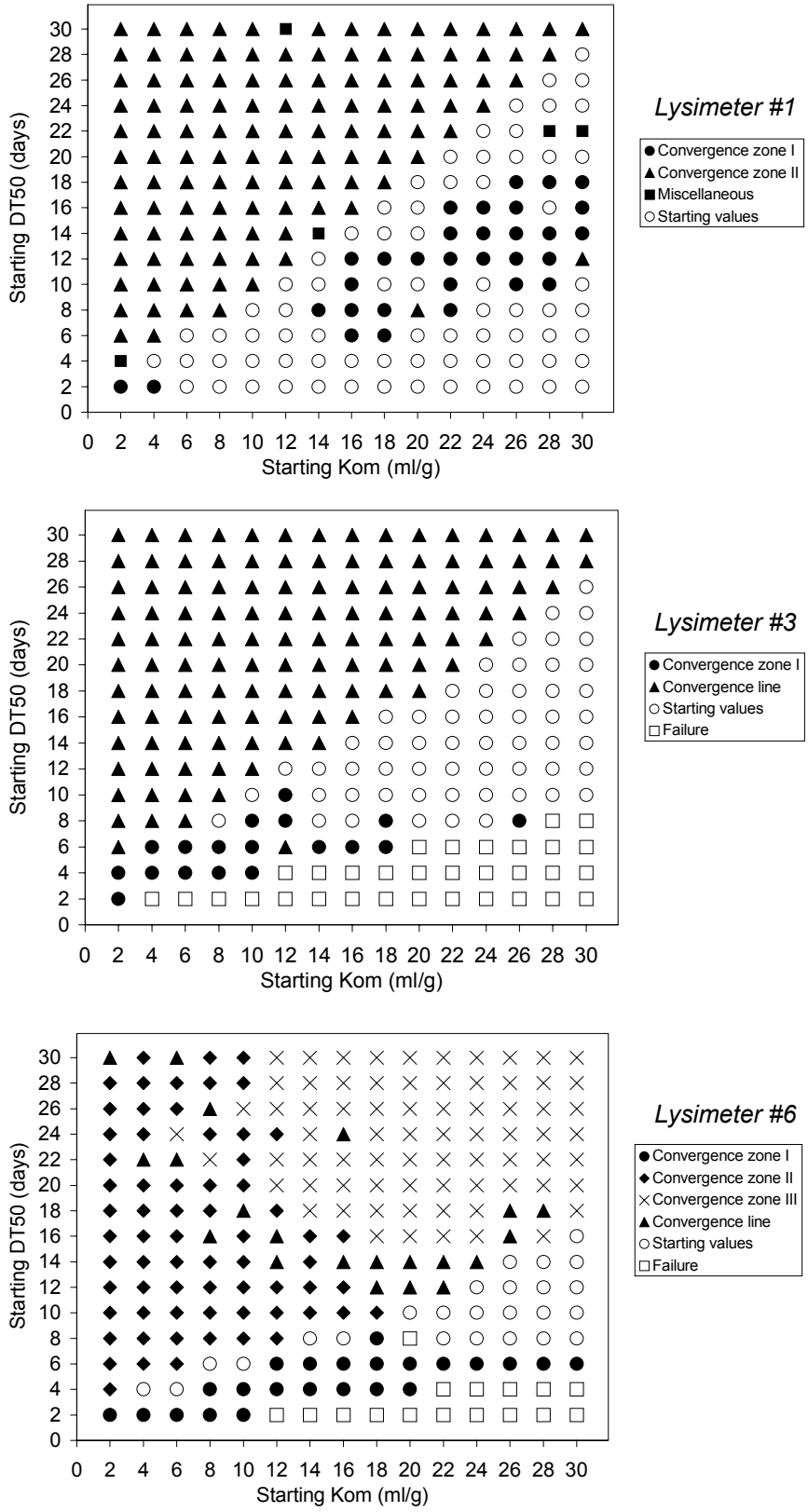

Figure 6-7. Dependence of the calibration outcome on the position of starting values in the Kom - DT50 parameter space.

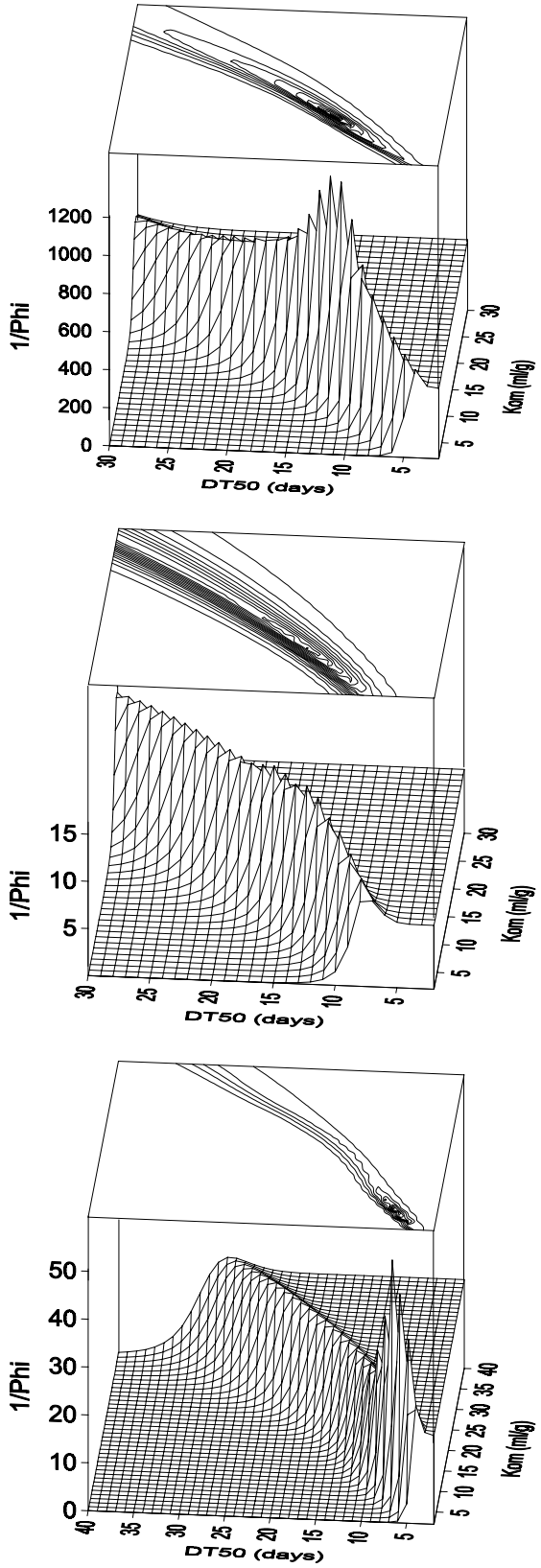

Figure 6-8. Surface and contour plots showing the goodness-of-fit to the experimental data (Φ^{-1}) for multiple combinations of Kom and DT50. Each grid node represents a PESTRAS run for the corresponding combination of Kom and DT50.

Chapter 7

DISCUSSION & PERSPECTIVES

THE ROLE OF SENSITIVITY ANALYSIS IN PESTICIDE FATE MODELLING

Comprehensive sensitivity analyses were carried out for leaching models used for pesticide registration in Europe and results were presented in Chapters 3 and 4. Sensitivity results were relatively similar for the four models (Chapter 3). Predictions for volumes of water percolated at 1m-depth were only marginally affected by input parameters included in the analysis and the main driver of the water balance is expected to be the meteorological data fed into the model, *i.e.* rainfall and potential evapotranspiration data. In contrast, predictions for pesticide loss by leaching were influenced by a large number of input parameters and to a much greater extent. In most scenarios considered, the models were most sensitive to parameters related to sorption and degradation. In a small number of scenarios, hydrological parameters were found to have a large influence on predictions for pesticide loss as well.

Parameters describing sorption (the Freundlich distribution coefficient and exponent) and degradation (degradation rates or half-lives) are particularly uncertain (Dubus *et al.*, 2001). A factor of variation of two was attributed to nominal values in the sensitivity analyses (Chapters 3 and 4) to represent the uncertainty in these parameters. Uncertainty may arise from i) natural variability in environmental conditions; ii) variability and bias in experimental and analysis procedures associated with the determination of sorption and degradation properties; and, iii) the use of linear or non-linear fitting to derive these parameters. Results from the sensitivity analyses suggest that this uncertainty will be magnified through the modelling process and predictions from pesticide leaching models should hence be considered largely uncertain. A number of recent initiatives (ECOFRAM, 1999; EUPRA, 2001)

have suggested that probabilistic approaches based on Monte Carlo simulations should be used in pesticide fate modelling to account for parameter uncertainty. Information on model sensitivity can be combined with knowledge on parameter uncertainty to select those parameters that should be included in both model calibration and probabilistic modelling. Chapters 3 and 4 suggest that these modelling activities should concentrate on varying sorption and degradation parameters.

Sensitivity analyses were carried out using i) a one-at-a-time approach where each parameter is varied one after the other, all other parameters being kept constant at their nominal value; and ii) a procedure based on Monte Carlo sampling where random sequences of input parameter values are linearly related to model output. Results of the latter approach have only been presented for MACRO in the present thesis (Chapter 4). The Monte Carlo approach is often used to study the sensitivity of environmental fate models (Hamby, 1995). However, results obtained in the present research question the appropriateness of the Monte Carlo approach for studying the sensitivity of pesticide leaching models. Issues have been raised in Chapter 4 with regard to i) the linearisation of the relationship between model input and output for these highly non-linear models; and ii) the influence on sensitivity results of the attribution of different probability density functions. Additional investigations have been performed since the paper corresponding to Chapter 4 was accepted for publication. The research investigated the influence on sensitivity results of the use of different seed numbers. Seed numbers are used to initiate the generation of random sequences in Monte Carlo sampling. A sensitivity analysis for PELMO for the scenario involving Pesticide 1 in the Wick soil (see Chapter 3 for details of the scenario) was carried out using the Monte Carlo approach described in Chapter 4 and repeated 10 times with different seed numbers obtained through random sampling into a uniform distribution (range [1;1000]). Table 7-1 presents sensitivity rankings for the 10 replicated sensitivity analyses. Seed numbers were found to have a strong impact on the ranking of parameters according to their influence on predictions for pesticide loss, although the most influential parameters remained the same (Figure 7-1). The specific application of Monte Carlo approaches

to study the sensitivity of pesticide leaching models should be investigated further. One-at-a-time and Monte Carlo approaches are complementary and should therefore be used in combination where possible. For instance, in the case of the prediction of pesticide loss, a Monte Carlo approach could be used to identify those parameters which most influence model predictions and the impact of these parameters could then be investigated in detail by drawing a number of pesticide breakthrough curves for different input values (one-at-a-time approach).

In the sensitivity analyses reported in the present document, most parameters were considered to be independent. This assumption must be questioned since correlations between a number of input parameters can be expected, especially i) between sorption and degradation parameters in general; ii) between parameters describing water retention curves in PESTLA / PEARL and MACRO; and iii) between parameters defining the boundary between micropores and macropores in MACRO. The issue of independent variation of hydraulic parameters has been partly addressed in Chapter 4 where it was demonstrated that the independent variation of individual parameters of the Brooks and Corey equation within the Monte Carlo simulations led to a population of water retention curves that was broadly representative of the uncertainty associated with the water retention data. A framework for automating the derivation of MACRO hydraulic parameters from a few key variables ('meta-parameters') has been recently developed by the candidate (Figure 7-2) and is currently being used to i) assess the sensitivity of this model; and, ii) calibrate the model against lysimeter data using parameter estimation techniques based on Monte Carlo sampling. More research is needed on the practical combination of parameter values and on its influence on sensitivity and calibration results.

CALIBRATION OF PESTICIDE LEACHING MODELS: WHERE TO GO NEXT?

Calibration of models plays an important role in modelling the fate of pesticides as it helps to i) establish the 'validation' status of pesticide leaching models; ii) get a good fit between model predictions and the experimental data; iii) establish the basis for subsequent extrapolation; and, iv) estimate sorption and degradation parameters representative of field conditions. Although calibration is in many ways a cornerstone in the simulation of pesticide leaching, it has received little attention in the past.

Part of the work presented in this thesis investigated the robustness of the inverse modelling approach which may present possibilities to estimate sorption and degradation parameters from field data. Different combinations of optimised Kom and DT50 were found to provide a similar fit to the observed patterns of pesticide concentrations in lysimeter leachate for the three lysimeters considered. The two parameters were shown to compensate for one another in the modelling and this may hamper the identification of values for these parameters by inverse modelling against data for pesticide concentrations only. Correlation between model input parameters is not limited to sorption and degradation parameters in the complex models that are used to simulate pesticide leaching and non-uniqueness in calibration results is therefore likely to occur widely. Sorption and degradation parameters have probably played the role of fitting parameters in the calibrations undertaken and have probably integrated inaccuracies and deficiencies in the structure of the model, its parameterisation and in the experimental data. The research hence established that non-uniqueness is likely to occur when pesticide leaching models are calibrated against leaching data only and that parameters may lose their physical, chemical or biological meaning through the calibration process.

In light of the research reported here, estimates of sorption and degradation properties obtained by an inverse modelling approach should be considered with care in the assessment of the environmental fate of pesticides, especially within the scope

of pesticide registration. Combinations of optimised parameters may be coincidental to some extent because of the ill-posed nature of the calibration problem and because the parameters to be optimised may function as fitting variables in the calibration. Non-uniqueness in calibration should be investigated in each calibration exercise aimed at estimating values for sorption and degradation parameters. These findings also question the appropriateness of using calibration in the evaluation of pesticide leaching models.

It is proposed that research is conducted into the following aspects of the calibration of pesticide leaching models:

- the identification of data requirements for calibration;
- the specific evaluation of a number of parameter estimation approaches;
- the assessment of methodologies recognising non-uniqueness as a property of the modelling system.

The suggestions for research are discussed in more detail below.

The Identification of Data Requirements for Calibrating Pesticide Leaching Models

The use of numerous combinations of starting values for the calibration of the PESTRAS model (Chapter 6) demonstrated that non-uniqueness existed in the calibration of this model against data for pesticide concentrations from lysimeter experiments. Non-uniqueness in the results may have originated from i) the failure of the inverse modelling package to find a suitable minimum in the objective function; or, ii) the use of data that did not permit a robust and independent estimation of sorption and degradation parameters. Lattice modelling demonstrated that non-uniqueness could be mainly attributed to this latter aspect. The shape of the error surface suggested that the parameters Koc and DT50 compensated for one another in the prediction of pesticide leaching data and that the data used would not allow for a differentiation between sorption and degradation parameters in the calibration exercises. Additional research is needed to identify those data that are

required to allow a robust estimation of Koc and DT50 values from experimental data through inverse modelling.

A parallel can be drawn with the research that was conducted in the field of soil physics when data requirements for a robust estimation of soil hydraulic properties (*i.e.* the soil water retention and unsaturated hydraulic conductivity curves) were identified (Hopmans & Simunek, 1999). The use of inverse methods for determining unsaturated flow parameters from transient experiments had first been reported by Zachmann *et al.* (1981; 1982). It was demonstrated that the use of water outflow data only from one-step outflow experiments was insufficient to allow a robust parameter estimation (Kool *et al.*, 1985; Toorman *et al.*, 1992) and that the use of additional flow-controlled data, such as independently measured soil water retention data (van Dam *et al.*, 1992) or soil water tension values (Kool & Parker, 1988; Toorman *et al.*, 1992), were needed to stabilise the inverse problem.

An approach similar to that followed in soil physics should be applied to pesticide fate modelling to enable the reduction in non-uniqueness in the calibration of pesticide leaching models and to enhance confidence in parameter values estimated through an inverse modelling approach. Data requirements for a well-posed problem can be identified through i) careful examination of governing equations; ii) trial-and-error investigations or response surface analysis using combinations of synthetic or field data (Toorman *et al.*, 1992); or, iii) experimental design (Simunek *et al.*, 1998). The use of synthetic data, *i.e.* data that have been generated by the model, is usually preferred over field measurements because i) 'true' values of the parameters are known; ii) no measurement error is associated with the calibration data, which limits the uncertainty in the analysis of the inverse problem; and, iii) a relatively small noise in the data is sufficient to aggravate the likelihood of the ill-posedness of the inverse problem (Russo *et al.*, 1991). Stochastic and deterministic errors can also be superimposed on synthetic data to provide a closer representation of field conditions (Simunek & de Vos, 1999; Pan & Wu, 1999). Response surface analysis, of which lattice modelling is a particular type, has been shown to be a particularly effective method for identifying data requirements for calibration and for assessing the

robustness of non-linear estimation algorithms (Kool *et al.*, 1985; Russo *et al.*, 1991; Simunek & van Genuchten, 1996; Simunek *et al.*, 1998). Sensitivity analysis has been shown to be a useful tool for designing optimal sampling schemes (Kool & Parker, 1988). In theory, experiments should be designed to maximise the sensitivity to all parameters, but the simultaneous optimisation of a large number of parameters is not practically feasible. A more useful approach is hence to design the experiment so that direct information on the least sensitive parameters is obtained thereby allowing either the removal of these parameters from the estimation process or the provision of good starting values for these parameters.

The Specific Evaluation of Parameter Estimation Approaches for Pesticide Leaching Models

A range of techniques have been developed for parameter estimation in other fields of science and those techniques which meet the technical requirements for a robust calibration of pesticide leaching models should be evaluated. The most promising techniques for estimating parameter values for pesticide leaching models are discussed below.

Response surface analysis

The present research demonstrated that lattice modelling is a useful tool for investigating issues of non-uniqueness in the estimation of sorption and degradation parameters from field leaching data (Chapter 6). Since the technique provides the modeller with the basis for a detailed analysis of the error surface, it can help to anticipate the behaviour of non-linear estimation algorithms and can also be seen as an efficient alternative to such algorithms where non-uniqueness is expected. However, the usefulness of lattice modelling for parameter estimation problems other than that presented here may be limited to situations where a small number of parameters are optimised because of i) the large increase in computational requirements when additional parameters are considered; and, ii) the difficulties associated with the visualisation of multidimensional parameter spaces in more than

three dimensions. The first limitation can be overcome by replacing the systematic incremental variation of each parameter (which is at the basis of the large computational requirements of lattice modelling) by an efficient random sampling scheme providing a good coverage of the parameter space. Latin Hypercube Sampling (LHS; McKay *et al.*, 1979) is recognised as an efficient stratified sampling scheme (Hamby, 1994) and its efficiency within the context of surface error analysis could be further enhanced by considering replicated LHS random sets generated using different seed numbers. This would provide a more intense coverage of the parameter space for parameter estimation while keeping the number of runs to a minimum. The second limitation arising from difficulties in visualising multidimensional spaces can be addressed by plotting model output against each parameter (scatter plots) or combinations of two parameters (3-D charts or contour plots; Toorman *et al.*, 1992). Representations of parameter planes in 2 or 3 dimensions only provide cross-sections of the full multidimensional parameter space and can hence only give an indication of the multidimensional behaviour of the objective function. However, they provide a useful approximation of the response surface (Simunek *et al.*, 1998). The use of Principal Component Analysis as a complementary approach to these representations deserves investigation as it provides an efficient way to deal with multidimensional parameter spaces in lower dimension spaces within a statistical framework.

Parameter estimation techniques based on the calculation of derivatives

The present research on parameter estimation was carried out using the *PEST* package (Doherty, 2000). PEST is a versatile software that can be linked to virtually any simulation model since it only interacts with the model through its input and output files. The fact that PEST does not require any model recoding is of particular importance in the pesticide registration context since standard and agreed models are used to estimate the environmental fate of contaminants. Any alteration to the code of a model would mean that the coding may have to be checked independently and the new model evaluated against benchmark model predictions or experimental data. The non-linear parameter estimation procedure implemented in PEST is based on a

modified Gauss-Levenberg- Marquardt algorithm (Doherty, 2000). The other model-independent package which is widely used in parameter estimation, especially in groundwater flow modelling, is *UCODE* (Poeter & Hill, 1998). UCODE is an open-source project from the US Geological Survey and the inversing algorithm is based on the modified Gauss-Newton procedure (Hill, 1998). PEST and UCODE have both been demonstrated to work well for a range of groundwater flow inverse problems (Poeter & Hill, 1997). Both programs rely on the calculation of model derivatives to find their way through the multidimensional parameter space ('hill-climbing techniques') and the performance of the two packages will be greatly dependent on the accuracy of these derivatives (Poeter & Hill, 1998; Dieses, 1999; Doherty, 2000). This accuracy will mainly be determined by the implicit characteristics of the model from a numerical perspective (number of significant figures used in internal calculations, discretization, internal rounding, precision in output files) since both packages are model-independent and are typically used without model recoding. Improved procedures for parameter estimation relying on the calculation of model derivatives have recently been proposed although they have not been designed for distribution as stand-alone packages. These include: i) ECOFIT (Dieses, 1999), a modified version of the generalised Gauss-Newton approach, which has been used to estimate water transport parameters from data on water contents from a field study; ii) SUSE (Gottesbüren *et al.*, 1996), a package developed by BASF AG which has been linked to modified versions of the pesticide leaching models PELMO and PEARL; and, iii) an approach combining simulated annealing and downhill-simplex procedures (Pan & Wu, 1999). Although all these approaches have been shown to enable a robust estimation of model input parameters in some instances, they are likely to under-perform within the context of regulatory modelling since the characteristics of simulation models considered in exposure assessment will lead to inaccuracies in the calculation of derivatives. The assessment of parameter estimation techniques for calibrating pesticide leaching should therefore probably concentrate on those procedures which do not require the calculation of derivatives. Inverse procedures which meet this criterion and which are considered of interest for the calibration of pesticide leaching models include SUFI (Abbaspour

et al., 1997) and other techniques based on Monte Carlo sampling (Ducheyne & Feyen, 1999) or Genetic Algorithms (Takeshita & Kohno, 1999).

Probabilistic parameter estimation techniques

The Sequential Uncertainty domain parameter FItting (SUFI) is a method aimed at estimating parameter values using a Monte Carlo stratified sampling approach within a Bayesian framework (Abbaspour *et al.*, 1997). The procedure starts with the attribution of statistical functions describing the broad uncertainty associated with an initial estimation of parameter values. Each probability density function is then divided into a number of equal strata and the first moment of each stratum on the parameter scale is taken to represent that stratum. Each stratum is attributed a score which is initially set to zero. In the exhaustive mode, the model is run for all combinations of all possible strata for each parameter. If constraints exist with regard to the computational requirements, only a random subset of the list of possible combinations is run. These procedures allow the uncertainty in input parameters to be propagated through the model. A goal function which can integrate measurement error is then calculated on the basis of the model results. If a given tolerance criterion is met, then the strata corresponding to the model run is given a 'hit' and will see its score increased by one unit. When all runs are completed, a frequency distribution of hits is constructed for each stratum. Strata having a small score at both ends of each interval are eliminated, thus providing an updated uncertainty domain for each parameter for the next iteration. The procedure is repeated iteratively until a tolerance criterion is met. At each iteration, the uncertainty domain for each parameter will get smaller and the goal function will be decreased. The initial prior information characterising the uncertainty in model input parameters is gradually updated to result in a reduced posterior state of belief. SUFI is hence a parameter estimation procedure which is sequential, operates within uncertainty bounds, employs only forward modelling and is iterative (Abbaspour *et al.*, 1997). There is no theoretical constraint on the number of parameters which can be estimated through this procedure although limitations will arise from computational requirements. The procedure is general and was found to be stable and always

convergent in a number of applications (Abbaspour *et al.*, 1997; 1999). However, optimised results were also found to be largely affected by the output variables included in the objective function (Abbaspour *et al.*, 1999) and by the inherent capability of the model to describe the field data (Abbapour *et al.*, 2000). SUFI is considered as a promising technique with regard to parameter estimation for pesticide leaching models.

Another method which does not rely on the calculation of model derivatives and which integrates probabilistic components is that initially proposed by Keesman & van Straten (1988). In this method, a Monte Carlo sensitivity analysis similar to that reported in Chapter 4 is first carried out to identify those parameters to be optimised through calibration. An iterative Monte Carlo search of the parameter space referred to as *RORASC* (ROtated RAndom SCan) is then used. The iterative method is based on applying rotations and transformations of the parameter space (Janssen & Heuberger, 1995b) to identify parameter values which lead to a minimisation of an error function. Probability density functions initially assigned to parameters on the basis of expert judgement or literature information are updated during the optimisation process and this enables the estimation of i) confidence intervals on estimated values; and, ii) the uncertainty associated with model predictions following calibration by the RORASC procedure. Ducheyne & Feyen (1999) applied the procedure to estimate values for eight input parameters of the contaminant transport model WAVE (Vanclooster *et al.*, 1994) using nitrate leaching data. WAVE integrates subroutines describing the main processes affecting the fate of reactive solutes and is used in Belgium for assessing the environmental fate of pesticides. The procedure was found to be efficient and led to a decrease in the overall uncertainty in the simulation of field data (Ducheyne & Feyen, 1999).

Genetic Algorithms (GAs) are generally considered a promising technique for parameter estimation. GAs are based on the mechanics of natural selection and natural genetics, which combine artificial survival of the fittest with genetic operators (*e.g.* selection, crossover and mutation) abstracted from nature (Goldberg, 1989). Typically, the GA search for an optimum combination of parameter values

will begin with a population of parameter realisations generated by random sampling, as opposed to more traditional optimisation techniques which consider a single combination of parameter values. Rules for parameter perturbation are probabilistic and GAs use the objective function directly without recurring to model derivatives. GA search procedures have been successfully applied to i) estimate soil hydraulic parameters from outflow and tensiometric data (Takeshita & Kohno, 1999); ii) estimate rate parameters of kinetic models (Moros *et al.*, 1996; Park *et al.*, 1997); and, iii) calibrate water quality (Mulligan & Brown, 1998) and groundwater flow models (Karpouzos *et al.*, 2001) . Takeshita & Kohno (1999) consider that GAs would be most beneficial for highly non-linear models, such as contaminant transport models.

Other aspects related to optimisation procedures which deserve investigation

Whatever the numerical or probabilistic algorithms used for model calibration, the assessment of the fit between model output and field data will rely on the calculation of an objective function. In pesticide fate modelling, the estimation by an individual of the general adequacy between model simulations and field data is often based on a visual comparison between measured and simulated data for a number of sampling points during the course of the experiment. The complex nature of this process is unlikely to be reflected by a simple calculation of the weighted sums of residuals which is frequently used as a goodness-of-fit measurement. It is therefore proposed that more complex statistics integrating different aspects of the fit between simulated and measured data are critically assessed. Within the scope of pesticide leaching, these could integrate the overall pesticide leaching, the shape of the chemograph, peak as well as low concentrations and the timing of events. Madsen (2000) reported an inversion procedure based on a multiple objective function for describing water hydrographs that can be readily applied to the calibration of pesticide leaching models. The integration of different model outputs in an objective function will help to stabilise the inverse problem as demonstrated by Toorman *et al.* (1992).

A modeller will nearly always have an opinion about what a reasonable value for a particular parameter should be or the expected range for this parameter. This knowledge may originate i) from guidance on model parameterisation provided in user manuals; ii) from previous experience with the model or with the attribution of values to this parameter; or, iii) from earlier modelling and calibration exercises reported in the literature. It is important that this knowledge is integrated into the parameter estimation procedure. Educated guesses about parameters can be specified in model calibration through the attribution of variation ranges and numerical relationships between parameters, as in PEST and UCODE, or through the attribution of statistical distributions to input parameters for probabilistic approaches to calibration. In the latter case, the statistical functions will be updated through the model calibration process and these techniques can therefore be considered Bayesian in nature. More generally, prior information can be integrated effectively into objective functions using likelihood measures associated with penalty scoring (Russo *et al.*, 1991). Although the incorporation of prior information into the inverse problem can worsen the fit in some instances, the procedure generally leads to more stable and reliable parameter estimates (Simunek *et al.*, 1998) and hence a decrease in the uncertainty associated with the estimated parameters (Yeh, 1986). Procedures for integrating expert knowledge into the calibration should be critically reviewed within the context of pesticide fate modelling.

The inverse problem is said to be properly posed if and only if: i) a solution exists; ii) the solution is unique for any set of outputs; and, iii) the solution is stable (Carrera & Neuman, 1986). With regard to the research proposed here, identifiability aspects should be guaranteed by the identification of data requirements for the calibration of pesticide leaching models while non-uniqueness and stability issues will be addressed through the evaluation of procedures for estimating parameters efficiently.

Recognising Non-Uniqueness as a Property of the Modelling System

Traditional parameter estimation procedures such as those presented above are based on the assumptions that there is a correct model of the processes of interest and that

an optimum set of input parameters exists which is superior to other input combinations (Schultz *et al.*, 1999). These procedures are therefore concerned with identifying the optimum parameter set. However, there is ample evidence in the literature that numerous inverse problems are ill-posed (Yakowitz & Duckstein, 1980; Hornung, 1996; Weiss & Smith, 1998) and that multiple sets of parameters might produce a similar fit to the data (Zak *et al.*, 1997; Romanowicz & Beven, 1998; Beven & Freer, 2001; Chapter 6). This has been referred to as 'equifinality' (Beven, 1993). Equifinality generally results in conventional calibration algorithms returning different optimised combinations of parameters depending on starting values supplied as initial parameter estimates (Pan & Wu, 1999).

The Generalised Likelihood Uncertainty Estimation (GLUE) methodology proposed by Beven and Binley (1992) is based on the rejection of the concept of an optimal parameter set and the acceptance of equifinality in model calibration. The principle of the approach is i) to identify those parameter sets which provide an acceptable fit to the data ('behavioural parameter sets'); and, ii) to weight behavioural parameter sets according to their associated likelihood in order to estimate the uncertainty in the modelling resulting from equifinality. The identification of behavioural parameter sets is based on traditional Monte Carlo sampling into predefined statistical functions attributed to each parameter and the running of the model many times (typically, a few 10,000 runs). A likelihood function is calculated on the basis of model output for each model run. Parameter sets giving a likelihood below a specific threshold level are considered to be 'non-behavioural' and assigned a likelihood of zero. The likelihood measures of the runs are then rescaled so that their cumulative total is one and the retained model predictions are weighted according to the new likelihood measures for each specific parameter set. The weighted model predictions can be presented in the form of a cumulative distribution function and percentiles representing the uncertainty in the model and that resulting from the calibration can be extracted. The procedure is considered Bayesian since the rescaled likelihood functions (or degree of belief) may be combined with some prior likelihood associated with parameter sets using Bayes theorem (Lee, 1989) to result in a posterior likelihood function. In practice, the prior likelihood will often take the

form of a uniform distribution and no refinement of the likelihood functions through the Bayes theorem will take place (Schultz *et al.*, 1999).

The candidate has initiated early work on the estimation of the extent of equifinality in the calibration of pesticide leaching models. Investigations initially concentrated on the PESTLA model. Equifinality was assessed in the context of the calibration of the model against synthetic data. The 'experimental' data were leaching concentrations predicted by PESTLA for the first base-case scenario (Pesticide 1 on Wick series) in Chapter 3. A total of four parameters (the distribution coefficient normalised to organic matter Kom, the Freundlich exponent nf, the molar activation energy of degradation EGCV and the half-life DT50) were attributed uniform distributions and 30,700 values were sampled using non-stratified Monte Carlo sampling. Sampled values were used to create PESTLA input files and the model was run for each of these inputs. The selection of the four parameters to be included in the analysis was based on sensitivity results reported in Chapter 3 for PESTLA. The likelihood function was defined using a sum of squared residuals between 'measured' and simulated annual concentrations which was transformed to allow likelihoods to vary between 0 and 1. The charts presenting likelihood against the four parameters are presented in Figure 7-3. The charts demonstrate that a large number of PESTLA runs may result in a similar fit to the experimental data. Given the basic similarities in pesticide leaching models, it may thus be expected that equifinality is widespread in pesticide fate modelling. 'Behavioural' runs were obtained across the range of variations applied to the four input parameters, except for Kom for which runs with likelihoods close to one were unlikely for Kom values over ca. 17.5 ml/g. These results extend the findings presented in Chapter 6 to a four-dimensional parameter space. As outlined by Schultz *et al.* (1999), the inclusion of additional input parameters in the GLUE methodology is likely to show increased equifinality since this provides additional flexibility with regard to the description of the data.

The GLUE methodology is interesting in that it provides a framework for dealing with the concept of equifinality, itself likely to be widespread in environmental modelling (Beven & Freer, 2001). However, the approach is limited in that i)

computational requirements are large and typically have to be addressed through parallel processing; and, ii) results will be greatly influenced by a number of subjective choices (Beven, 2001). Decisions which have to be made relate to the selection of parameter ranges for each input parameter, the definition of the likelihood function used to assess goodness-of-fit and the selection of threshold criteria for segregating behavioural from non-behavioural runs (Schultz *et al.*, 1999). Although the whole procedure may be attractive, the large dependence of results on these choices is likely to limit the potential application of the GLUE methodology in pesticide fate modelling.

SETTING RESEARCH PRIORITIES

The research proposed is fairly significant in terms of work and there is therefore a need for prioritising research activities.

It is considered that the main priority is to build on the research reported in the present PhD thesis to establish the extent of non-uniqueness associated with current procedures for the calibration of pesticide leaching models. Emphasis should be placed on calibrations involving more than two parameters and may focus either on the calibration of the water balance or prediction for pesticide loss. It is recommended that error surface analysis is adopted. It is anticipated that the research will show that non-uniqueness is widespread in the calibration of leaching models.

The second step in the research programme should be to identify whether additional data collected in the field would help to reduce calibration non-uniqueness. The data which could be used in the calibration may include soil water content and tension measurements at a number of depths or data on pesticide residues at different times during the experiment. Requirements for a robust calibration can be established through error surface analysis using experimental design or trial-and-error approaches. It is recommended that initial investigations concentrate on synthetic

data, *i.e.* data generated by forward modelling. Research that is closely related to this point is the identification of goodness-of-fit criteria which would enable the complete description of hydrographs and chemographs.

Provided that the research conducted has demonstrated that calibration uniqueness is achievable, additional research should be undertaken to identify automatic calibration procedures that would enable a robust identification of minima in error functions. Approaches based on probabilistic considerations are likely to perform better than classical approaches. The latter procedures typically require precise calculation of model derivatives, but this will be constrained by the nature of the pesticide leaching models used for registration in Europe.

If the research has demonstrated that equifinality is widespread in pesticide fate modelling, *i.e.* that multiple combinations of parameter inputs will provide a similar fit to the data, then the GLUE methodology which propagates the uncertainty associated with calibration to model predictions should be investigated. However, it is anticipated that its use in the context of registration modelling would be subject to much debate as the outcome of the approach is largely dependent on a number of subjective choices made during its implementation.

GENERAL CONCLUSIONS

Complex deterministic models are being used in Europe to assess the potential for a pesticide to impact on the environment. Within the context of pesticide registration, calibration may be used to test the ability of pesticide fate models to provide an adequate reflection of pesticide behaviour in the field, to help in the parameterisation of these complex models, to estimate appropriate values for selected parameters or to establish the basis for subsequent extrapolation to different environmental conditions. Despite being a cornerstone in pesticide fate modelling, the process of calibration has received little attention in the past.

Sensitivity analyses were carried out for leaching models used for pesticide registration in Europe. Predictions for volumes of water percolated at 1m-depth were only marginally affected by input parameters included in the analysis and the main driver of the water balance is expected to be the meteorological data fed into the model, *i.e.* rainfall and potential evapotranspiration data. In contrast, predictions for pesticide loss by leaching were influenced by a large number of input parameters and to a much greater extent. In most scenarios considered, the models were most sensitive to parameters related to sorption and degradation of the pesticide. In a small number of scenarios, hydrological parameters were found to have a large influence on predictions for pesticide loss as well. Sensitivity analysis proved to be an effective approach not only for ranking parameters according to their influence on model predictions, but also for investigating model behaviour in a more general context. However, the research questioned the robustness of the Monte Carlo approach to sensitivity analysis as issues of replicability were uncovered.

Inverse modelling exercises carried out within the scope of the PhD demonstrated that non-uniqueness is likely to be widespread in the calibration of pesticide leaching models. Correlation between parameters within the modelling, such as that between sorption and degradation parameters when predicting pesticide leaching, may prevent the robust derivation of values through an inverse modelling approach. Depending on the calibration system considered, these parameters may act as fitting variables and integrate inaccuracies, uncertainties and limitations associated with experimental data, modelling and calibration. A special implementation of error surface analysis termed lattice modelling was proposed in the PhD as an efficient technique to i) assess the likely extent of non-uniqueness issues in the calibration of pesticide leaching models; and, ii) replace traditional parameter estimation procedures where non-uniqueness is expected.

The present PhD has brought significant new knowledge on model sensitivity and calibration through the running of pesticide leaching models for numerous occurrences, as opposed to current modelling practices which are mostly based on a single or few model run(s). Investigations undertaken have revealed that non-

uniqueness in calibration is likely to be widespread. Combined with the fact that pesticide leaching models are largely sensitive to changes in input parameters and that critical parameters are largely uncertain, this confirms that predictions of pesticide leaching models are uncertain and should be considered with care. Nevertheless, pesticide fate modelling will remain a key tool in pesticide registration because of its flexibility and time- and cost-effectiveness when compared to field investigations. Issues of uncertainty present a challenge which if properly addressed can greatly strengthen the modelling process. Model calibration is a multifaceted activity which brings together knowledge on pesticide fate, experimental investigations and numerical modelling. Increased confidence in modelling predictions will come from both the identification of data requirements for robust calibration and improvement in calibration practices.

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Table 7-1. Monte-Carlo sensitivity analyses for PELMO for 10 random samples using different seed numbers. The SRRC is the Standardised Ranked Regression Coefficient for each parameter. SRCC in italics indicate significance at p<0.05. Smaller rank numbers indicate greater influence on PELMO predictions for pesticide loss. Parameters are described in Appendix 3.1.

	#1		#2		#3		#4		#5		#6		#7		#8		#9		#10	
	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank	SRRC	Rank
DEGR	*-0.684*	1	*-0.643*	1	*-0.678*	1	*-0.655*	1	*-0.647*	1	*-0.639*	1	*-0.637*	1	*-0.674*	1	*-0.638*	1	*-0.666*	1
KF	*-0.577*	2	*-0.547*	2	*-0.528*	2	*-0.544*	2	*-0.531*	2	*-0.565*	2	*-0.515*	2	*-0.603*	2	*-0.540*	2	*-0.594*	2
QTEN	*0.333*	3	*0.284*	3	*0.300*	3	*0.312*	3	*0.316*	3	*0.304*	3	*0.301*	3	*0.300*	4	*0.279*	3	*0.312*	3
NF	*0.238*	4	*0.238*	4	*0.224*	4	*0.261*	4	*0.255*	4	*0.234*	4	*0.227*	4	*0.302*	3	*0.226*	4	*0.247*	4
WC_FC	*-0.174*	5	*-0.134*	5	*-0.144*	5	*-0.145*	5	*-0.133*	5	*-0.148*	5	*-0.153*	5	*-0.151*	5	*-0.145*	5	*-0.161*	5
BUD	*-0.094*	7	*-0.105*	6	*-0.110*	6	*-0.084*	7	*-0.067*	7	*-0.090*	6	*-0.094*	6	*-0.048*	7	*-0.073*	6	*-0.108*	7
MEXP	*0.099*	6	*0.072*	7	*0.070*	7	*0.089*	6	*0.097*	6	*0.061*	7	*0.063*	7	*0.070*	6	*0.054*	7	*0.113*	6
AMXD	*-0.056*	8	-0.025	9	-0.021	10	*-0.070*	8	-0.013	11	*-0.028*	8	-0.010	10	-0.010	13	-0.033	8	-0.021	11
UPTK	-0.019	10	-0.021	10	-0.008	14	-0.027	11	-0.023	9	-0.009	12	*-0.041*	8	0.012	12	0.002	16	-0.018	12
PDRA	-0.003	16	-0.019	11	-0.004	16	*0.033*	9	0.022	10	-0.027	9	-0.004	13	*0.044*	8	0.020	9	-0.011	13
OC	-0.010	14	0.010	14	0.023	8	0.009	16	*-0.029*	8	-0.025	10	0.005	12	-0.015	11	0.011	10	0.004	16
CINT	-0.010	13	-0.017	12	-0.022	9	-0.021	14	-0.006	15	0.003	17	*-0.033*	9	-0.003	16	*-0.006*	13	-0.023	9
FEXT	0.015	11	0.000	17	0.016	11	0.024	12	-0.004	16	-0.004	16	0.003	14	-0.010	14	-0.008	11	*0.044*	8
ANET	0.002	17	0.010	13	0.009	13	-0.023	13	-0.011	13	-0.008	13	-0.007	11	-0.001	17	-0.006	12	0.022	10
PH	0.012	12	*0.033*	8	0.004	17	0.001	17	0.012	12	-0.006	14	-0.001	17	-0.016	10	-0.006	14	-0.010	14
COVM	0.003	15	-0.001	16	0.004	15	-0.029	10	0.001	17	0.014	11	-0.002	16	0.026	9	0.003	15	0.003	17
WP	*-0.028*	9	-0.004	15	-0.015	12	0.010	15	0.008	14	0.005	15	-0.002	15	-0.005	15	-0.002	17	0.004	15
R^2	0.957		0.952		0.933		0.944		0.954		0.956		0.957		0.928		0.941		0.945	

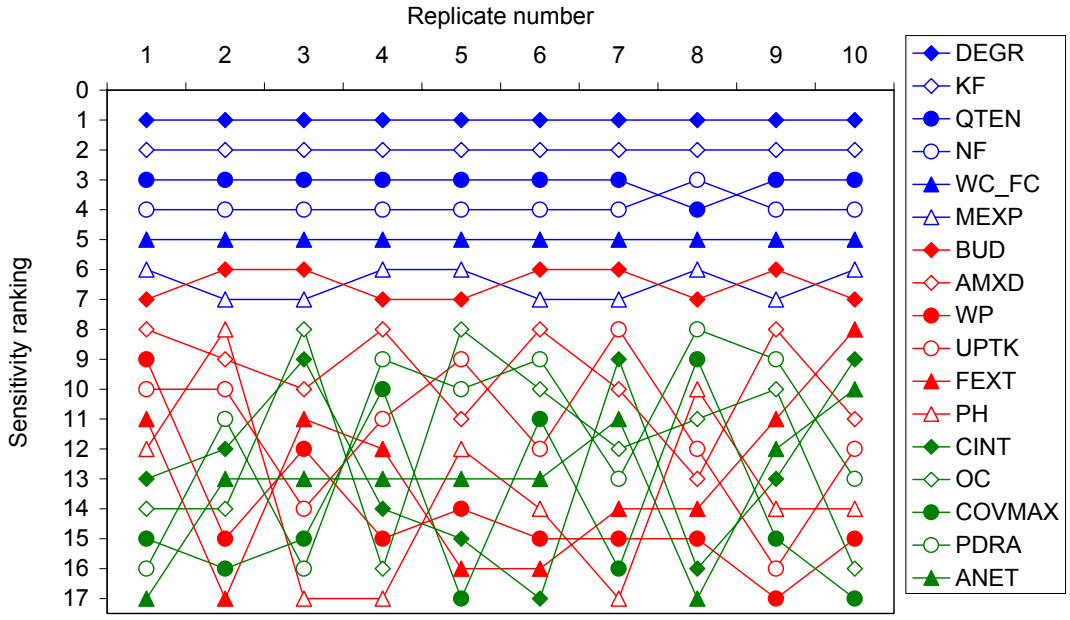

Figure 7-1. Influence on sensitivity results of the seed number used in random sequence generation for Monte Carlo sensitivity analyses for PELMO. Ten different seed numbers were used. Parameters are ranked according to their Standardised Ranked Regression Coefficients. Smaller rank numbers indicate greater influence on PELMO predictions for pesticide loss. Parameters are described in Appendix 3.1.

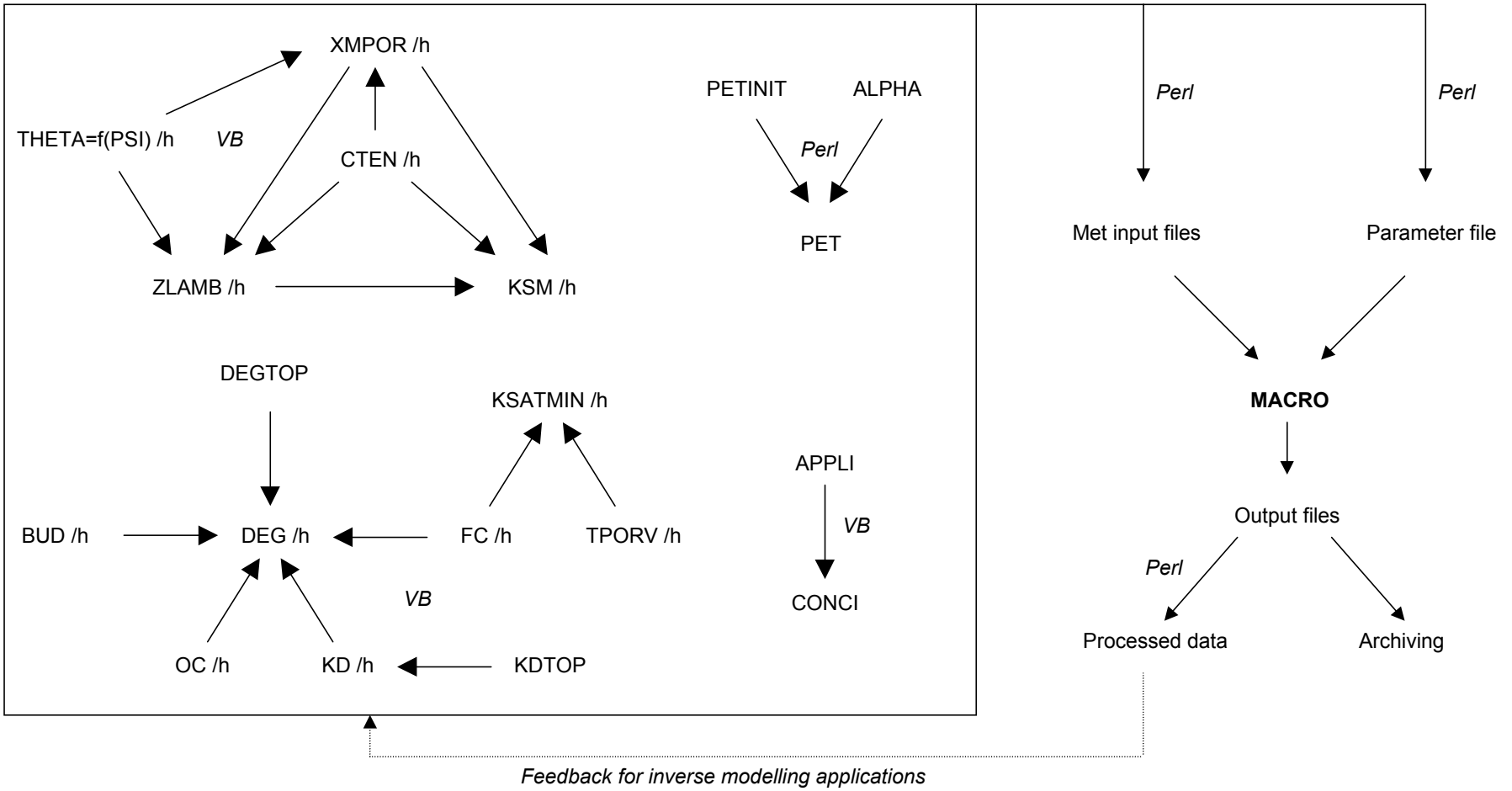

Figure 7-2. Schematic representation of the procedures enabling automated modelling with MACRO. Parameter estimation routines, input file generation, model running and output processing are fully automated using a combination of PERL and VB programming. The package can be used indifferently for sensitivity analysis, inverse modelling and probabilistic modelling applications.

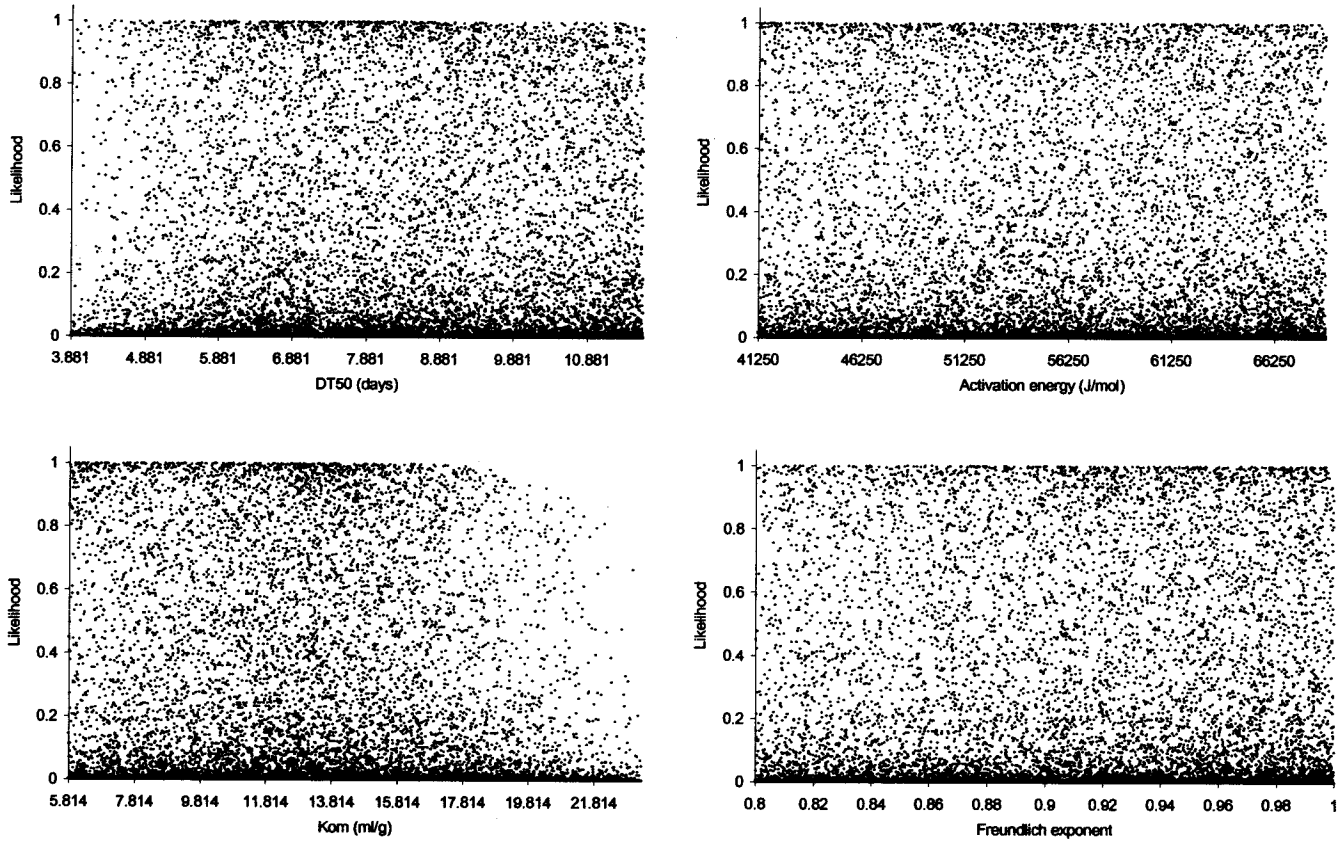

Figure 7-3. Equifinality plots showing likelihood against selected parameters. Parameters were sampled in uniform distributions using non-stratified Monte Carlo sampling. Results of 30,700 PESTLA runs are presented. Larger likelihoods indicate a better fit to the experimental data.

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