

An Improved Dual-Permeability Model of Solute Transport in Structured Soils

**Model Development and Parameter Identification in
Laboratory and Field Experiments**

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Abstract

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Preferential flow through macropores is one of the major pathways through which pesticides can leave the root zone and enter ground and surface waters. Dual-permeability models account for preferential flow by including a separate flow domain coupled to the less permeable soil matrix. The exchange of water and solutes between flow domains is usually described by first-order expressions. Key model parameters regulating the degree of preferential flow are difficult or impossible to derive from direct measurements. Therefore, the objective was to evaluate the possibilities of parameter identification through automatic calibration in the dual-permeability model MACRO. An improved version of the model, with implicit numerical solutions introduced to shorten model run times, was first developed. This enabled the use of computationally intensive calibration methods. Generalised likelihood uncertainty estimation (GLUE) and sequential uncertainty domain parameter fitting (SUFI) were applied to a comprehensive field data set containing measurements of soil water contents, drainflow and flux and resident concentrations of bentazone and bromide. All groups of data were needed to get highly conditioned and unbiased parameter estimates. However, the parameter describing mass exchange between pore domains was poorly conditioned even with a very comprehensive data set. SUFI decreased the initial uncertainty domains significantly for all parameters except for the parameter describing mass exchange between pore domains in the subsoil. However, random sampling from SUFI posterior uncertainty domains resulted in larger prediction uncertainty compared to GLUE. This is because these domains contain parameter combinations that are poor simulators, mainly due to parameter correlations. GLUE and a parameter identification method based on the localisation of information (PIMLI) were applied to real and numerically generated data from laboratory microlysimeter experiments. The data contained enough information to reduce the uncertainty of the parameter describing mass exchange between pore domains, the saturated matrix hydraulic conductivity and the macroporosity. Simultaneous identification of the macroporosity, the macropore hydraulic conductivity and the parameter describing macropore tortuosity was not possible, probably because of parameter correlations. Measurements with large information content for parameter identification were generally found during the first irrigations after solute application.

Keywords: pesticides, parameter identification, parameter uncertainty, calibration, dual-permeability model, macropore flow, MACRO, GLUE, SUFI, PIMLI.

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Appendix

This thesis is based on the following papers, which are referred to in the text by their Roman numerals

- I. Larsbo, M., Roulier, S., Stenemo, F., Kasteel, R. & Jarvis, N. An Improved Dual-Permeability Model of Water Flow and Solute Transport in the Vadose Zone. *Vadose Zone Journal*, In Press.
- II. Larsbo, M. and Jarvis, N. Information content of measurements from tracer microlysimeter experiments designed for parameter identification in dual-permeability models. *Manuscript*.
- III. Larsbo, M. & Jarvis, N. 2005. Simulating solute transport in a structured field soil: Uncertainty in parameter identification and predictions. *Journal of Environmental Quality* 34, 621-634.

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In Paper I, I had the main responsibility for the writing. The fifth author contributed to the Introduction and the Materials and Methods sections. I did all the Fortran programming of the new numerical solutions in the model and conducted the parameter identification exercise. I also did the comparison with the analytical solution to the kinematic wave equation. In Paper II, I was responsible for the writing, chose all methods and carried out all the analysis. In Paper III, I initiated the study, carried out all the analysis and had the main responsibility for the writing.

Introduction

Residues of pesticides used in agriculture have been found in surface waters and groundwater both in Europe (Leistra & Bouten, 1989) and the USA (Barbash *et al.*, 2001) at concentrations that often exceed the EU drinking water limit of $0.1 \mu\text{g l}^{-1}$. These findings have led to public concern about environmental and health effects from the intensive use of pesticides. Aquatic ecosystems near agricultural land are at risk of being negatively affected by pesticide residues. The toxicological effects remain uncertain in many cases, but the risk that contaminated ground or surface water used for human consumption might cause health problems even at concentrations below the drinking water limit cannot be ruled out.

Modern pesticides are usually thoroughly tested in the laboratory and in the field before they are approved for use in agriculture. Based on results from laboratory experiments, pesticides were expected to stay in the root zone where they have the potential to be beneficial to the crop and where the degradation rate is usually high. However, the occurrence of pesticides in groundwater during the last twenty years has revealed limitations in the understanding of transport processes in the soil.

Today, a number of pathways through which pesticides can leave the root zone and enter ground and surface water have been identified. Leaching through soils is considered to be of major importance for the occurrence of pesticides in groundwater (Flury, 1996). It has been shown that a fraction of the pesticide can move below the root zone and appear in tile drains much earlier than would be expected from classical theories. High concentrations of pesticides in drainflow have been observed within weeks of application (Kladivko *et al.*, 1991; Brown *et al.*, 1995; Larsson & Jarvis, 1999). One rain event can even be enough to cause leaching through tile drains independent of the sorption and degradation characteristics of the solute (Kladivko *et al.*, 1991). One important reason why the classical theories fail is that they do not account for preferential flow. Apart from leaching, runoff can carry pesticides from agricultural fields to lakes and rivers and spray drift and volatilisation of pesticides can cause direct pollution of surface waters. In addition to these major pathways, point sources originating from improper handling of pesticides, for example during filling of sprayers, can significantly contribute to contamination of ground and surface water (Kreuger & Nilsson, 2001).

Simulation models are important tools for analysis of water flow and solute transport in the vadose zone. They can be used to test single process descriptions, to study system responses when many processes are interacting and to extrapolate both in time and space, where multiple measurements would be impractical. This makes the use of simulation models for assessment of pesticide leaching an attractive option. The EU directive 91/414 suggests that simulation models should be used to assess the leaching risk within the EU. However, experimental data are essential for model development, for evaluating the accuracy of models and thus for assessing the confidence that should be placed in model predictions. As the understanding of the processes governing the transport of pesticides through soil has increased, the models have become more complex, but all models are

simplifications of real systems and model estimations are always wrong to some extent. A test of twelve European pesticide leaching models against data from four field experiments showed that the subjectivity in the process of parameter estimation and input selection is critical (Boesten, 2000). Therefore, the transparency of the modelling process is the basis for 'good modelling practice' (Vanclouster *et al.*, 2000).

Theoretical background

Preferential flow

Preferential flow occurs when water and solutes move predominantly through a limited part of the soil, largely bypassing the soil matrix (Jarvis, 2002). Preferential flow thus reduces the residence time of solutes in the unsaturated zone and limits the contact with reactive soil materials, which leads to slower degradation and less sorption of contaminants. Water and solutes may move to far greater depths, and much faster, than would be predicted by Richards' equation. An important feature of preferential flow is its non-equilibrium nature resulting from the short time available for equilibration between preferential flow paths and the bulk of the soil matrix. One of the causes of preferential flow is macropores created by earthworms, shrinking of drying soils, decayed root channels or voids in naturally aggregated soils. There are many definitions of macropores in the literature (Beven and Germann, 1982). In this thesis a macropore is simply defined as a pore that, when water filled, results in preferential flow. Macropores usually have a larger impact on water flow and solute transport in fine-textured soils but can occur in many types of soils (Flury *et al.*, 1994). Macropore flow will occur whenever the precipitation at the soil surface exceeds the infiltration capacity of the soil micropore domain (Fig. 1). Clay & Stott (1973) and Rao *et al.* (1974) were among the first to introduce preferential flow as an explanation for elevated concentrations of pesticides found in the subsoil. It is now widely accepted that preferential flow often has a large impact on the transport of solutes through structured soils (Flury, 1996).

Although preferential flow implies a potential risk for elevated concentrations of pesticides below the root zone, it may sometimes reduce leaching of solutes. Shipitalo *et al.* (1990) showed that a low-intensity irrigation shortly after application reduced leaching of atrazine, bromide and strontium ions. They argued that the solutes were washed into the soil by the first irrigation and thereby partly protected from the preferential flow created in the subsequent irrigations. Larsson & Jarvis (2000) demonstrated the same effect for some very mobile pesticides in a modelling exercise.

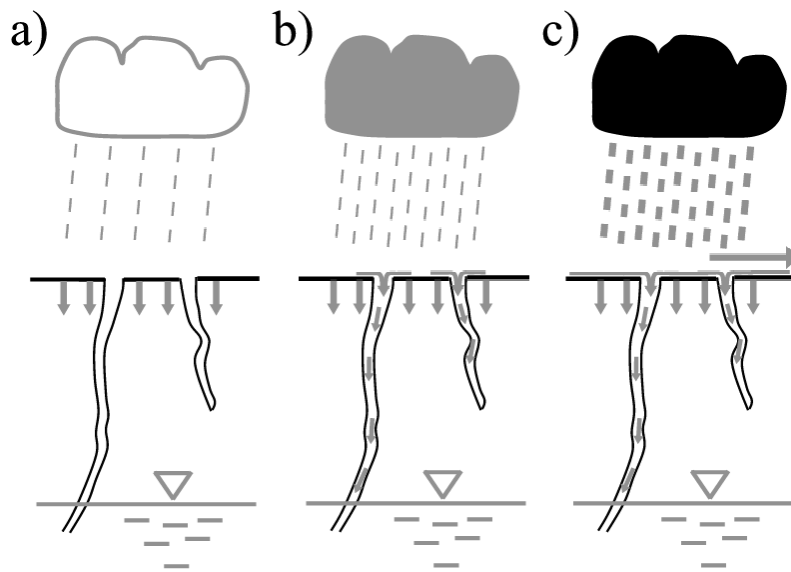


Fig. 1. Generation of macropore flow and runoff: a) rain intensity is smaller than the matrix infiltration capacity, b) rain intensity exceeds the matrix infiltration capacity causing macropore flow that can transport surface applied solutes to the ground water, bypassing the soil matrix, and c) rain intensity exceeds the total soil infiltration capacity causing runoff.

Preferential flow models

Preferential flow in structured soils can be described by a variety of dual-porosity (van Genuchten & Wierenga, 1976), dual-permeability (Gerke & van Genuchten, 1993a, Jarvis, 1994) or multi-porosity/permeability (Gwo *et al.*, 1995) models. Dual-porosity and dual-permeability models divide the soil into two interacting regions, one associated with the macropore system and one with the micropore system. Dual-porosity models assume that the water in the micropores is stagnant while dual-permeability models allow flow in both regions. Within each group, models differ mainly in the descriptions of water flow in the pore regions and the transfer of water and solutes between pore domains. One widely used dual-permeability model is MACRO (Jarvis, 1994; Larsbo & Jarvis, 2003), which uses Richards' equation to describe water flow in micropores and a modified kinematic wave equation to describe water flow in macropores. Reviews of the most popular preferential flow modelling approaches are given in Feyen *et al.* (1998) and Šimůnek *et al.* (2003). Compared to single pore domain models, preferential flow models require additional parameters to describe the dual or multi pore domains. These parameters are sometimes difficult or impossible to derive from direct measurements.

Exchange between pore domains

Fick's diffusion law is assumed to govern the transfer of solutes from a saturated macropore into a stagnant micropore domain. Fick's law in one dimension is given by:

$$\frac{\partial C_{mic}}{\partial t} = D \frac{\partial^2 C_{mic}}{\partial x^2} \quad [1]$$

where C_{mic} (kg m^{-3}) is the solute concentration in the micropores, t (s) is time, D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient corrected for pore tortuosity and x (m) is the horizontal coordinate. The implementation of Fick's law into models of water flow and solute transport demands detailed information on the geometry of the soil aggregates and the macropore structure, which is difficult or impossible to obtain. Therefore, the concept of first-order mass transfer (FOMT), which is also mathematically simpler to implement than Fickian diffusion, has often been used to describe solute transfer between macropores and micropores in dual-porosity (van Genuchten & Wierenga, 1976; Vanclouster *et al.*, 1996) and dual-permeability models (Gerke & van Genuchten 1993a; Larsbo & Jarvis, 2003). The FOMT term for solutes, Γ_s ($\text{kg m}^{-3} \text{s}^{-1}$) is given by:

$$\Gamma_s = \alpha_s (C_{mac} - C_{mic}) \quad [2]$$

where α_s (s^{-1}) is the FOMT coefficient for solutes, reflecting the geometry of the pore system and C_{mac} (kg m^{-3}) is the solute concentration in the macropores. These models use an average solute concentration in the stagnant or low-permeability soil matrix, thus neglecting within-aggregate gradients. The effects of these simplifications have been studied for some important cases. Griffioen (1998) compared analytical solutions to Fick's diffusion law in one dimension and FOMT for cyclic mass transfer into and out of an immobile zone. He concluded that FOMT was unsuitable when the time for filling was short. Jørgensen *et al.* (2004) compared the FOMT concept as implemented in the analytical dual porosity model CXTFIT with a numerical solution to the two-dimensional form of Fick's diffusion law in the discrete fracture/matrix diffusion model FRACTRAN (Sudicky & McLaren, 1992), using data from saturated large undisturbed column experiments. Both approaches could accurately simulate the breakthrough of bromide but the FOMT coefficient had to be recalibrated for different flow rates and durations of bromide pulses.

Figure 2 illustrates the effects of the simplifications in FOMT for different time scales for one-dimensional diffusion of a non-reactive solute in a stagnant zone. Step changes of the solute concentration at the boundary were used and the initial concentration in the stagnant zone was zero. The average concentration in the stagnant zone calculated by Fick's diffusion law could be well simulated with FOMT when the FOMT coefficient was optimised by minimising the root mean square error for the whole simulation period (Fig. 2a). When the time scale was

reduced ten times, the average concentration was poorly simulated by FOMT using the same FOMT coefficient (Fig. 2b).

The assumption of stagnant water in the micropores will in most cases not be valid. In these cases, the water transfer between pore domains can be viewed as a process, which at least mathematically, is similar to diffusion of solutes. The equation for horizontal one-dimensional water flow is given by:

$$C \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial x} \left[K \frac{\partial \psi}{\partial x} \right] \quad [3]$$

where C (m^{-1}) is the differential water capacity $\partial \theta / \partial \psi$ and K (m s^{-1}) is the hydraulic conductivity in the micropore domain.

First-order mass transfer has been used to model water exchange in dual-permeability models (Gerke & van Genuchten, 1993a; Larsbo & Jarvis, 2003). The equation for FOMT of water, Γ_w (s^{-1}), which is mathematically identical to Eq [2], is given by Gerke & van Genuchten (1993a) as:

$$\Gamma_w = \alpha_w (\psi_{mac} - \psi_{mic}) \quad [4]$$

where α_w ($\text{m}^{-1} \text{s}^{-1}$) is the FOMT coefficient for water, ψ_{mic} (m) and ψ_{mac} (m) are the average pressure potentials in the micropores and in the macropores respectively. The driving force for water transfer can also be given as a difference in water contents (Larsbo & Jarvis, 2003). This approach is further described in the *Materials and methods* chapter. Again, the FOMT coefficient is dependent on the geometry of the pore system, the time scale and the initial conditions.

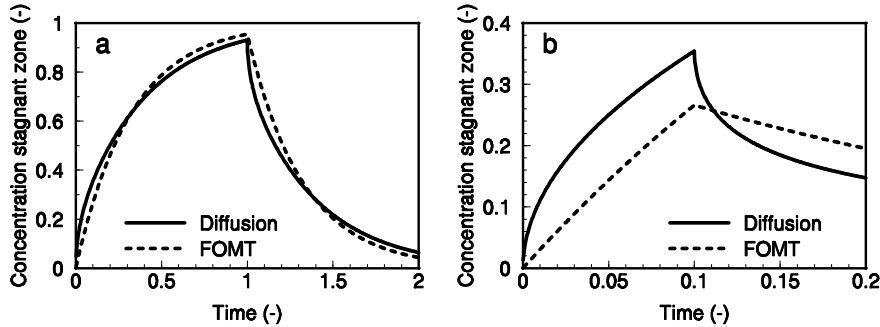


Fig. 2. Comparison of Fick's diffusion law and first-order mass transfer (FOMT), both written in dimensionless form, for different time scales for step changes in solute concentration at the stagnant zone boundary, a) simulation time = 2 and b) simulation time = 0.2. The FOMT coefficient used in both a and b was optimised by minimising the root mean square error for the whole simulation period used in a.

Wallach & Steenhuis (1998) pointed out that if a few preferential flow paths carry all the solutes and the width of the stagnant micropore domain between adjacent preferential paths is very large then the average concentration in the matrix will be very small most of the time and not suitable to use as the driving force for the solute exchange. The fact that the FOMT-coefficient is dependent on the time-scale and not only related to soil properties has implications for extrapolations from laboratory experiments to field conditions. Calibrated values from laboratory experiments will in general not be applicable for field conditions if the experimental setup differs from field conditions. However, the dependency of the FOMT-coefficient on the time-scale is largest in the beginning of the solute infiltration period when only the concentration in a thin layer close to the macropore is influenced (Griffioen, 1998). The relatively large uncertainty in calibrated values for the FOMT coefficient for these cases will probably have little significance regarding leaching since most of the solute bypasses the soil matrix anyway.

Despite the above-mentioned problems, different kinds of FOMT formulations are frequently used to describe mass transfer between pore regions in structured soils (Šimůnek *et al.*, 2003) because the data needed to justify the higher degree of complexity for models based on Fick's law is often lacking. Gerke & van Genuchten (1993b) argued that FOMT is sufficiently accurate for water exchange for most practical purposes when considering the large uncertainties involved in modelling and measuring preferential flow processes. Šimůnek *et al.* (2003) considered accurate coupling of the macropore and micropore domains to be one of the greatest challenges in preferential flow modelling. They highlighted the different hydraulic properties of micropore-macropore interfaces compared to the bulk of the micropores (Thoma, Gallegos & Smith, 1992). These differences further reduce the possibilities to use direct measurements to determine the FOMT coefficient.

Parameter sensitivity and uncertainty

The degree of influence of input parameters on model estimations can be assessed through sensitivity analysis. A parameter is considered sensitive if a change in a parameter value results in a large change in the model estimations. Parameter sensitivity has often been stated mathematically by the sensitivity coefficient:

$$S_i = \frac{\partial y}{\partial x_i} \cong \frac{\Delta y}{\Delta x_i} \quad [5]$$

where y is the model estimation and x_i is an input parameter. Sensitivity analysis is conducted for a number of reasons, among others to determine (i) which parameters contribute most to the output variability, (ii) which parameters are insignificant and can be eliminated from the model, (iii) whether parameters interact and (iv) the initial parameter intervals for use in a subsequent calibration.

Parameter uncertainty originates for example from uncertainty in measured values, spatial and temporal variability and uncertainty in the derivation of parameter values from primary data (Dubus, Brown & Beulke, 2003). Parameter uncertainty can be accounted for by the use of a parameter distribution around the expected value instead of the use of a single value.

Calibration

Calibration has become a cornerstone in water flow and solute transport modelling (Dubus, Beulke & Brown, 2002). Calibration refers to the process of determining parameter values based on comparisons of model outputs and measurements. Given the larger number of parameters and the difficulties to derive parameter values from direct measurements, the requirement for calibration appears particularly important for preferential flow models.

Traditionally, calibration has been done by ‘trial-and-error’, where one parameter at a time is changed and the model fit to experimental data is evaluated by visual inspection. Although the trial-and-error method can be useful, especially when the data is scarce or of low quality, it is highly subjective and demands a high degree of expert judgement. Therefore, this type of calibration has largely been abandoned in favour of less subjective automatic methods. The principle underlying automatic calibration is the minimisation of an objective function through the modification of input parameters. The objective function is given as a function of the residuals, the differences between observed and estimated values. A number of objective functions have been suggested (Loague & Green, 1991). Two frequently used objective functions are the root mean square error and the model efficiency (EF). In the case of multiple data sets (*e.g.* resident and effluent concentrations), the objective function has to be formulated as a multi-objective function. The model efficiency is given here as an example:

$$EF_{tot} = \sum_{i=1}^m w_i \frac{\sum_{j=1}^n (O_{ij} - \bar{O}_i)^2 - \sum_{j=1}^n (O_{ij} - P_{ij})^2}{\sum_{j=1}^n (O_{ij} - \bar{O}_i)^2} \quad [6]$$

where w_i is the weight given to each data set, m is the number of data sets, n is the number of observations in each group, O_{ij} and P_{ij} are the observed and simulated values, and \bar{O}_i is the average of the observations for each group. The weights are constrained by:

$$\sum_{i=1}^m w_i = 1 \quad [7]$$

Both the choice of objective function and, in case of multiple data sets, the way weights are assigned are subjective. This type of goodness-of-fit measure does not

take temporal offsets of model estimates against measurements into account. A difference in timing that may have little effect on, for example, accumulated leaching may have a major effect on the objective function value (Armstrong *et al.*, 1996).

Three aspects generally determine the success of a calibration procedure: identifiability, stability and uniqueness. If more than one parameter set results in the same model response the parameters are not identifiable. Instability means that a small change in a measured value or an error in a fixed parameter leads to a large change in a calibrated parameter value. Uniqueness is the inverse of identifiability; if a given response leads to more than one set of parameters the inverse solution is non-unique. A reduction of the number of parameters included in the calibration will increase the identifiability. Pesticide leaching models are likely to be subject to non-uniqueness problems because of their non-linear character and internal correlations (Dubus, Beulke & Brown, 2002).

Even when it is possible to find a unique solution or to successfully reduce the parameter uncertainty through calibration, the problem of applicability of calibrated values remains. Parameters that do not have a physical, chemical or biological meaning can only be obtained by calibration. Dubus, Beulke & Brown (2002) argue that such calibrated values are only valid for the specific conditions in which they were derived and cannot be used to extrapolate.

Monte Carlo based methods

The ever-increasing power of modern computers and the development of efficient numerical solutions have enabled the use of computationally intensive methods for parameter identification and predictions. These methods have greatly increased the awareness of some general problems with parameter identification in highly complex models (Beven and Binley, 1992; Gupta, Sooroshian & Yapo, 1998).

Traditional statistical theory assumes that model outputs are linear functions of the parameter values within their uncertainty interval (Kuczera & Parent, 1998). This is often a poor approximation for the highly non-linear processes included in pesticide leaching models. A number of Monte Carlo based methods for parameter identification have been developed during the last fifteen years to address the limitations associated with traditional calibration strategies that aim to find optimal parameter values and confidence limits based on the assumption of linearity. One of these limitations is that it is often impossible to find a unique parameter set that results in a significantly better fit to measured data compared to others. This observation of 'equifinality' was the starting point for the development of the GLUE methodology (Beven & Binley, 1992), which is further described in *Materials and Methods*.

Using a probabilistic approach to calibration, the unknown model parameters are treated as random variables, distributed according to a probability distribution, which expresses the existing knowledge about parameter values. Given this 'prior' knowledge, new measurements can be used to calculate posterior parameter distributions according to Bayes' theorem (Box & Tiao, 1973), which describes the process of learning from experience:

$$p(\theta | y) = l(\theta | y)p(\theta) \quad [8]$$

where in our case, y is the vector of measurements, $p(\theta | y)$ is the posterior parameter probability distribution, $l(\theta | y)$ is a likelihood function for the parameters θ given y and $p(\theta)$ is the prior parameter probability distribution.

The Metropolis algorithm, which is the simplest example of Markov chain Monte Carlo sampling, has successfully been used for sampling of the posterior parameter distributions in hydrological models (Kuczera & Parent, 1998). The Metropolis algorithm generates samples from a random walk, which adapts to the true posterior distribution.

Multi-objective problems arise whenever there is more than one measurement and corresponding model output to consider in parameter optimisation. The improvement in the fit to one measurement often leads to the deterioration of the fit to others. This has usually been handled by lumping all measurement points into one objective function (see Eq. [6] and [7]). By doing this, weights are implicitly assigned to the measurements (Gupta, Sorooshian & Yapo, 1998). In the case of multiple data sets, a single objective function can still be used, but a decision about the importance of each data type must be made (Beven & Binley, 1992; Zak, Beven & Reynolds, 1997), which introduces another element of subjectivity into the procedure. A more sophisticated way to handle multi-objective problems was proposed by Gupta, Sorooshian & Yapo (1998). They argue that since the choice of objective function and the weights assigned to different data types are subjective, attention should be focused on finding a 'pareto' (or non-inferior) set of parameters. The pareto set has the properties that moving from a point within the pareto set to a point outside always leads to the deterioration in the model fit to at least one measurement. Furthermore, starting from any point outside the pareto set, there always exists at least one point within the pareto set that increases the fit to all measurements. Any point within the pareto set is in this respect 'better' than any point outside the pareto set. In hydrological modelling, the pareto-optimality concept has mainly been applied to rainfall-runoff models (Yapo, Gupta & Sorooshian, 1998; Vrugt *et al.* 2003).

The methods discussed above, that have been developed to better account for uncertainty in parameters and predictions, are themselves uncertain because subjective choices still have to be made, for example in the selection of method and objective function.

The research problem

Dual-permeability models are more parameter demanding than single pore domain models since extra parameters are needed to define the division and the exchange between pore domains. Many of the parameters regulating the degree of preferential flow are difficult or impossible to measure directly. Although preferential flow models are gaining in popularity, a more widespread use has been

hampered by these difficulties (Šimůnek *et al.*, 2003; Forum for the Coordination of Pesticide Leaching Models and Their Use, 2000).

Parameters that cannot be determined through direct measurements must be identified by some calibration method. In order to reduce the degree of subjectivity and to ascertain the reproducibility of the results, calibration is preferably done through some inverse modelling method. Many inverse modelling methods are computationally intensive, sometimes requiring such a large number of model runs for successful calibration that they become impractical. The use of inverse methods for parameter identification in dual-permeability models has to date been limited to only a few studies (Schwartz, Juo & McInnes, 2000; Kätterer *et al.*, 2001; Roulier & Jarvis, 2003a,b) partly because model run-times have been excessively long, especially for field applications. Although these studies have contributed to the understanding of parameter identifiability in dual-permeability models, a lot remains to be done. For example, Roulier & Jarvis (2003a) suggested that the possibility of improving parameter identification by different experimental setups needed to be examined, while Dubus, Beulke & Brown (2002) considered the identification of data requirements for effective and robust calibration of pesticide leaching models a research priority.

The dual-permeability model MACRO (Jarvis, 1994) is relatively parsimonious regarding the number of parameters (Šimůnek *et al.* 2003) but does include parameters that are difficult to measure directly. In addition to long run times caused by the small time steps needed to ensure stability of the explicit numerical solutions, the previous version of MACRO suffered from a coarse spatial resolution near the soil surface. In order to analyse the possibilities of parameter identification in the MACRO model these problems must first be solved.

Objectives

The objectives were: (i) to develop an improved dual-permeability model of solute transport in the vadose zone which can be used in computationally intensive automatic calibration procedures, (ii) to test the possibilities of identification of key model parameters regulating the degree of preferential flow under laboratory and field conditions, and (iii) to develop an efficient laboratory setup and an improved sampling scheme for identification of these parameters.

The MACRO model was used in all applications. To improve the performance of MACRO, explicit numerical solutions for Richards' equation, the convection-dispersion equation and the heat flow equation were replaced by standard implicit solutions, adapted for use in a dual-permeability model where this was necessary. Three different methods, all capable of dealing with parameter uncertainty, were used for parameter identification: sequential uncertainty domain parameter fitting (SUFI) (Abbaspour *et al.*, 1997), generalised likelihood uncertainty estimation (GLUE) (Beven & Binley, 1992), and the parameter identification method based on the localisation of information (PIMLI) (Vrugt, Bouten & Weerts, 2001). Both artificial and real laboratory data from transient tracer microlysimeter experiments were used to test the possibilities for parameter identification in the laboratory (Papers I and II). Data on drainflow and transport of the weakly sorbed herbicide

bentazone and bromide were used in a parameter identification exercise using field data (Paper III). PIMLI was used to identify the measurements containing most information for parameter identification in the laboratory microlysimeter setup (Paper II).

Materials and Methods

Model description and development of MACRO 5.1

The MACRO model is a one-dimensional, physically based, dual-permeability model for water flow and solute transport in the soil vadose zone. The total porosity is divided into micropores and macropores, characterised by different flow rates and solute concentrations. A schematic representation of the model processes is given in Fig. 3. Only aspects of specific interest in relation to the results presented in this thesis are presented here. A more detailed description of the model can be found in Larsbo & Jarvis (2003).

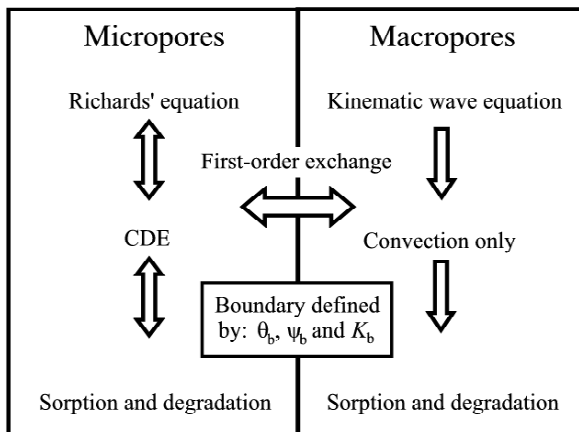


Fig. 3. Schematic representation of important process descriptions in MACRO. The symbols θ_b , ψ_b and K_b denote the saturated micropore water content, the boundary pressure potential and the saturated micropore hydraulic conductivity, CDE is the convection-dispersion equation.

Water flow

Water flow in the micropores is governed by Richards' equation (Richards, 1931) while water flow in the macropores, q_{mac} (m s^{-1}), is described by a modified kinematic wave approach (Germann, 1985), where the macropores are assumed to drain by gravity only. The hydraulic conductivity in the macropores, K_{mac} (m s^{-1}), is expressed as a power function of the macropore water content, θ_{mac} (-):

$$q_{mac} = K_{mac} = \left(K_{mac,sat} \right) \left(\frac{\theta_{mac}}{\theta_{mac,sat}} \right)^{n^*} \quad [9]$$

where $K_{mac,sat}$ ($m s^{-1}$) is the saturated conductivity of the macropores, $\theta_{mac,sat}$ (-) is the saturated macropore water content and n^* (-) is a 'kinematic' exponent reflecting macropore size distribution and tortuosity.

Solute transport

Solute transport in the micropores is calculated using the convection-dispersion equation with a first-order source-sink term representing mass exchange between flow domains. Convection is assumed to dominate solute transport in the macropores (*i.e.* dispersion is not explicitly accounted for).

The dual-permeability formulation

In the previous version of MACRO, the Brooks-Corey (1964) function was used to define the water content-pressure head relation in the micropores. The air-entry pressure parameter was used to define the pressure at the micropore-macropore boundary. In the new version, the Brooks-Corey function has been replaced by the van Genuchten (1980) function and the pressure at the micropore-macropore boundary is defined independently by an additional parameter. Both these changes increase the flexibility of the retention function, especially in the region close to saturation.

The saturated micropore water content (θ_b), the boundary pressure head (ψ_b) (Fig. 4) and the saturated micropore hydraulic conductivity (K_b) define the division between micropores and macropores. An additional point on the van Genuchten retention function defines the maximum water content allowed during one time step, $\theta_{max} = \theta_b + C_{mac}$, where C_{mac} (-) is the air-filled pore space in the macropores. The modified form of the van Genuchten retention function for the micropores is given by:

$$S = \frac{\theta_{mic} - \theta_r}{\theta_s^* - \theta_r} = \left(1 + |\alpha \psi|^N \right)^{-M} \quad [10]$$

where S (-) is the effective water content in the micropores, θ_{mic} (-) is the current micropore water content, θ_r (-) is the residual water content, θ_s^* (-) is a fictitious saturated water content, obtained by extrapolating the fitted water retention function to zero pressure, α (m^{-1}), N (-) and M (-) are shape parameters (where $M = 1 - 1/N$) and ψ (m) is the soil water pressure head.

Lateral water flow from macropores to micropores is described as a first-order approximation to the diffusion equation:

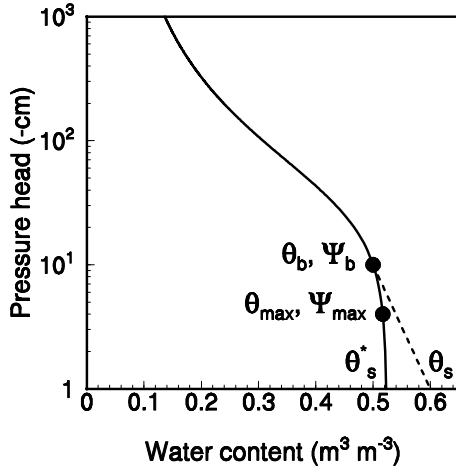


Fig. 4. Example of the modified van Genuchten water retention curve used in MACRO 5.1 for a fictitious soil (van Genuchten $\alpha = 0.03 \text{ cm}^{-1}$, van Genuchten $N = 1.5$, residual water content, $\theta_r = 0.0 \text{ m}^3 \text{ m}^{-3}$ and saturated micropore water content, $\theta_b = 0.5 \text{ m}^3 \text{ m}^{-3}$). The symbols θ_s (-) and θ_s^* denote the real and fictitious saturated water contents respectively.

$$S_w = \left(\frac{3 D_w \gamma_w}{d^2} \right) (\theta_b - \theta) \quad [11]$$

where d (m) is an effective diffusion pathlength related to aggregate size, γ_w (-) is a scaling factor introduced to match the approximate and exact solutions to the diffusion problem (Gerke and van Genuchten, 1993b) and D_w ($\text{m}^2 \text{ s}^{-1}$) is an effective water diffusivity given by:

$$D_w = \left(\frac{D_{\theta_b} + D_{\theta_{mic}}}{2} \right) \left(\frac{\theta_{mac}}{\theta_{mac,sat}} \right) \quad [12]$$

where D_{θ_b} ($\text{m}^2 \text{ s}^{-1}$) and $D_{\theta_{mic}}$ ($\text{m}^2 \text{ s}^{-1}$) are the water diffusivities at the saturated micropore water content and the current micropore water content respectively. A discussion on the validity of the first order mass transfer equation is presented in *Exchange between pore domains*. Water flow can occur in the reverse direction if the pressure potential in the micropores exceeds ψ_b . In this case, any water exceeding θ_b is instantly routed into the macropores.

The mass transfer term for solutes, U_e , accounts for both diffusion and convective flow:

$$U_e = \left(\frac{3 D_e \theta}{d^2} \right) (c_{mac} - c_{mic}) + S_w c' \quad [13]$$

where D_e ($\text{m}^2 \text{s}^{-1}$) is an effective diffusion coefficient, c_{mic} (kg m^{-3}) is the solute concentration in the liquid phase in micropores, c_{mac} (kg m^{-3}) is the solute concentration in the liquid phase in macropores, and c' (kg m^{-3}) indicates either the solute concentration in macropores or micropores, depending on the direction of water flow, S_w . The solute concentration in the water routed into the macropores at the soil surface is calculated assuming instantaneous equilibrium in a thin surface layer or mixing depth, z_{mix} (m).

Numerical solutions

The explicit numerical solutions used to solve Richards' equation, the convection-dispersion equation and the heat flow equation in the previous version of MACRO have been replaced with standard implicit solutions. These are described in Paper I and in Larsbo & Jarvis (2003). It was hypothesised that the superior stability of implicit solutions would allow larger time steps and hence reduce run times. The number of numerical layers in the previous version of MACRO was limited to twenty-two, which often led to a rather coarse spatial discretisation. In MACRO 5.1, the maximum number of numerical layers has been increased to two hundred, allowing for a much finer spatial discretisation and simulations of deep vadose zones.

The effects of nodal distance (numerical layer thickness) in the Richards' equation-based, numerical model SWAP were demonstrated by van Dam (2001). He compared simulations with nodal distances 1 and 5 cm to reference simulations with nodal distance 0.1 cm for infiltration into dry soils and evaporation from wet soils. He concluded that the use of nodal distances smaller than 1 cm, close to the soil surface, yielded acceptable simulation results while nodal distances of 5 cm severely overestimated infiltration and evaporation. The effect of nodal distance in simulations with the improved version of MACRO was tested for solute infiltration into a hypothetical dry clay soil. A non-reactive tracer was applied during one hour at a rate of $1.0 \text{ g m}^{-2} \text{ h}^{-1}$. The irrigation rate was 3.0 mm h^{-1} for the whole simulation period. Parameter values for the hypothetical soil are given in Table 1.

Table 1. *Parameter values for the hypothetical clay soil.*

| Parameter | Value |
|--|-------|
| Saturated micropore hydraulic conductivity, K_b (cm h^{-1}) | 0.1 |
| Boundary pressure head, ψ_b (-cm) | 10 |
| Saturated micropore water content, θ_b (%) | 45 |
| Saturated macropore water content, $\theta_{\text{mac,sat}}$ (%) | 3 |
| Residual water content, θ_r (%) | 5 |
| van Genuchten alfa, α (cm^{-1}) | 0.02 |
| van Genuchten N, N (-) | 1.1 |
| Mixing depth, z_{mix} (cm) | 0.1 |
| Inaccessible water due to anion exclusion, θ_{exc} (%) | 5 |
| Initial water content, θ_{mi} (%) | 30 |

Parameter identification methods

Four methods for evaluation of the possibilities of parameter identification in the MACRO model have been used in this thesis. These are briefly described in the following sections.

The Morris method

The Morris method (Morris, 1991) was developed as a preliminary screening tool for parameter sensitivity. He proposed a method comprising individually randomised one-factor-at-a-time designs. By screening entire prior uncertainty intervals the problems with non-linearity, encountered in classical one-at-a-time analysis (Hopmans & Šimůnek, 1999), are reduced. Before sampling, each parameter interval is divided into a number of equally large layers with the parameter values defined by the midpoints of each layer. To keep the number of model runs to a minimum, the scheme starts with the sampling of a base parameterisation, which is used in the calculation of one elementary effect for each parameter. The elementary effect, E , similar to the sensitivity coefficient (see Eq. [5]), for parameter i is defined as:

$$E_i(\mathbf{x}) = \frac{|\hat{y}(x_1, \dots, x_{i-1}, x_i + \Delta x_i, \dots, x_k) - \hat{y}(\mathbf{x})|}{\Delta x_i} \quad [14]$$

where Δx_i is the change in parameter $i = 1, \dots, k$, \hat{y} is a model output and \mathbf{x} is a base parameter vector. A large mean value of the elementary effects for parameter i indicates high sensitivity. A large measure of spread indicates a parameter involved in interactions or with non-linear effects. The base parameterisation is increased or decreased with equal probability, one-parameter-at-a-time. The sampling continues until all layers are used in a base case parameterisation.

GLUE

The generalized uncertainty estimation (GLUE) framework deals with model parameter and prediction uncertainty within the context of Monte Carlo analysis coupled with Bayesian estimation (Beven & Binley, 1992). The posterior parameter distribution is approximated by a discrete probability distribution, which can be used for predictions. Statistical measures, for example percentiles can be calculated from the posterior parameter distributions.

Usually, many parameter sets may equally well describe the observations according to some goodness-of-fit measure (objective function). Within the GLUE framework this is referred to as ‘equifinality’. If we accept this, it is not meaningful to search for unique parameter values. Therefore, the GLUE procedure is only concerned with evaluating the ‘likelihood’ of parameter sets as simulators of the observations. Likelihood is here used in a broad sense, meaning a specified measure of how well the outcome of a model and a parameter set describes the observations. Not all parameter sets will be acceptable simulators of the

observations. GLUE does not provide any information about parameter interactions, but these are implicitly reflected in the likelihood values.

The outcome of GLUE will, to some extent, be dependent on a number of subjective choices. Prior parameter distributions should be based on all available information, which is often limited to expert judgement and past experience. Beven & Binley (1992) consider it unlikely that this choice will be critical since new observations are supposed to dominate the posterior distribution. They suggest using a uniform prior distribution when information is lacking. The choice of objective function should reflect the available observations and the purpose for which the modelling is required. Finally, a threshold defining acceptable parameter sets needs to be defined. All non-acceptable parameter sets are discarded by assigning them zero weight.

Even though GLUE was designed to identify acceptable parameter sets, information on individual parameters can be obtained from cumulative posterior parameter distributions (Beven & Freer, 2001). These distributions give information on the degree of parameter conditioning. Parameters with distributions differing the most from the prior distributions have been most conditioned by the process.

Kuczera & Parent (1998) compared GLUE to Metropolis sampling for a simple water balance model for which the exact results were known. They showed that GLUE could produce misleading results unless a large number of samples were drawn. It should be noted that they used much fewer samples (3000) compared to most GLUE applications (20000-60000). The Metropolis sampling generated reliable results with modest sampling. Makowski, Wallach & Tremblay (2002) also made a comparison between the Metropolis algorithm and GLUE for parameter identification in a highly parameterised non-linear model. The results were similar for the two methods. The GLUE method has been criticised by Thiemann *et al.* (2001) for adopting a too liberal view of Bayesian statistics accepting just about any goodness-of-fit measure as a likelihood function.

GLUE has been shown to be useful for analysis of model parameterisation problems mainly with distributed hydrological models (Beven & Binley, 1992; Beven & Freer, 2001) but also with soil chemistry models (Zak, Beven & Reynolds, 1997; Zak & Beven, 1999) and nitrogen transport models (Schulz, Beven & Huwe, 1999). Because of the relatively large number of parameters and known uniqueness problems in preferential flow models (Roulier & Jarvis, 2003a, b), GLUE should be a potentially useful tool for analysing the possibilities of parameter identification in the MACRO model.

SUFI

Sequential uncertainty domain parameter fitting (SUFI) is a sequential, forward, iterative and Bayesian procedure for parameter fitting (Abbaspour *et al.*, 1997). SUFI begins with prior uncertainty domains of input parameters, which are subsequently reduced in an iterative procedure as the parameters become more conditioned by the measured data.

After defining prior uncertainty domains, these are divided into a number of equally large strata with the parameter value defined by the mid-point in each stratum. All combinations of parameter values are simulated in each iteration. Simulation results are then compared with observations through an objective function and the strata associated with the best values of the objective function are retained in the next iteration. A critical tolerance determines which strata are removed between iterations and a stopping rule determines when the iterative procedure is stopped. The remaining strata when the stopping rule is violated define the posterior uncertainty domains. As with GLUE, a number of subjective choices (the choice of objective function, critical tolerance and stopping rule) need to be made that are likely to influence the result.

SUFI has been used successfully for calibration of parameters in the van Genuchten/Mualem model for hydraulic parameters using data from multi-step outflow experiments (Abbaspour, Sonnleitner and Schulin, 1999). Roulier & Jarvis (2003a) used SUFI for calibration of the MACRO model using leaching data for MCPA and chloride measured in microlysimeter experiments. They concluded that SUFI gave reliable parameter estimates, when these could be checked with independent measurements.

PIMLI

Both SUFI and GLUE use one objective function calculated from the fit to all available measurements. One problem with this is that parameters often are insensitive to many of the measurements included. In that case, the ‘noise’ created by these measurements might overshadow the information contained in the measurements to which parameters are sensitive. The result is non-detectable or small responses to parameter changes in the objective function.

Vrugt, Bouten & Weertz (2001) and Vrugt *et al.* (2002) addressed this problem by developing a parameter identification method based on the localisation of information (PIMLI). The PIMLI procedure starts with Monte Carlo sampling of a pre-defined number of parameter sets from prior parameter distributions. These parameter sets are then executed through a model and subsequently categorized as ‘accepted’ or ‘non-accepted’ for each single measurement, depending on how well their corresponding estimation reproduces the measurement. Calculating the information content, IC, identifies the measured data containing most information for the identification of a parameter:

$$IC(m, p) = 1 - \frac{\sigma_{posterior}(m, p)}{\sigma_{prior}(p)} \quad [15]$$

where $\sigma_{posterior}(m, p)$ is the standard deviation of parameter p in the accepted parameter sets and $\sigma_{prior}(p)$ is the standard deviation of parameter p in the prior parameter distribution. If $IC(m, p)$ is close to zero, measurement m can be simulated equally well by any parameter value, indicating that m is non-informative for that parameter. If the information content is close to one, the accepted parameter values occupy a well-defined internal region of the prior distribution

indicating that m is informative for the parameter. When the measurements with highest IC are identified, these are used to constrain the parameters and to construct the posterior parameter distributions. These posterior distributions are sampled in the following iteration and the procedure repeated.

The smoothing effect of including many insensitive measurements is illustrated in Fig. 5, which shows dot plots of EF for different values of the macroporosity. All data, equally weighted between groups, was used in the calculation of EF in Fig. 5a, whereas only the ten measurements with the highest IC for the macroporosity were used in Fig. 5b. The prior parameter distributions for the hypothetical clay soil from Paper II were used. Using all the data results in positive EF values distributed over the whole uncertainty domain, whereas the use of the most informative measurements gives positive EF values distributed within a limited interval.

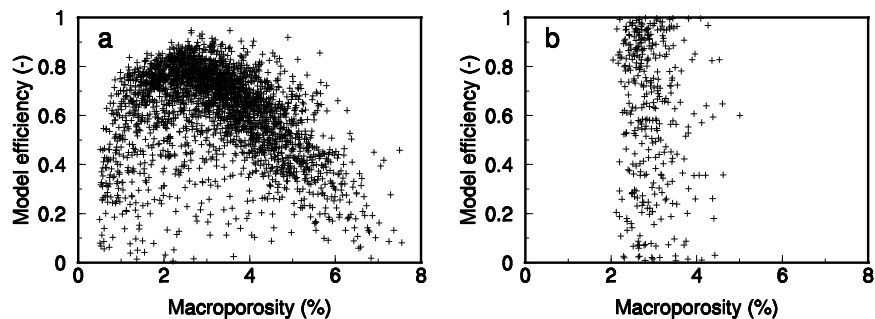


Fig. 5. Model efficiencies for different values of the macroporosity using all data (a) and the ten measurements with highest IC (b). Parameter values were sampled from a normal distribution with a mean value of 3 and a standard deviation of 1.5.

Experiments

In this thesis, the methods described in the previous section have been applied to data from both real and artificial microlysimeter experiments and to data from a field experiment carried out on a tile-drained clay soil.

The laboratory microlysimeter experiment

An experimental setup designed for parameter optimisation should include the measurements that are most sensitive to changes in the optimised parameter values (Hopmans and Šimůnek, 1999). It could be added that measurements that are sensitive to parameters not included in the optimisation should be excluded from a calibration exercise whenever possible. Otherwise there is a risk that posterior distributions of optimised parameters will be biased by errors in parameters not included. Moreover, the cost of laboratory experiments concerning sampling, sample analysis and time needed to carry out the experiments should be kept at a minimum.

I have been working with cylindrical soil samples, 20 cm high and with a radius of 9.6 cm. This size, referred to as microlysimeter, has several advantages compared to larger monoliths and smaller soil cores: (i) microlysimeter monoliths can be taken fairly easily with the use of a hydraulic pump and four hand-driven soil anchors, (ii) the size is usually large enough to represent the macropore structure of the soil, at least for agricultural topsoils, (iii) each soil horizon can often be sampled separately, which facilitates parameter identification, and (iv) the size of a microlysimeter is relatively small which means that many replicates can be run in a laboratory experiment. There are, on the other hand, some obvious disadvantages compared to larger sizes of lysimeters. As the size of a lysimeter decreases the risk that it does not represent the field characteristics of the soil increases. There is also a risk that continuous macropores are cut off by the walls of the lysimeter as the radius decreases or that the vertical continuity is overestimated because of the artificial bottom boundary.

A special irrigation chamber was constructed to facilitate the laboratory microlysimeter experiments. Twenty-four air atomising nozzles (Spraying Systems Inc.), each located 1.2 m above a microlysimeter, create a fine mist with low kinetic energy, which retains the structure of the soil surface throughout the experiment. The irrigation rate can be varied between 4 and 12 mm h⁻¹ dependent on the applied air and water pressure. Percolation samples are collected in plastic bottles connected to the microlysimeter bottoms through rubber hoses. A perforated base plate allows free drainage at the base of the column. A schematic sketch of the experimental setup is given in Fig. 6.

Microlysimeters and small soil cores (5 cm high and 3.5 cm radius) were collected from the topsoil of a heavy clay (defined as a Fluventic Eutrochrept in the USDA system) at Ultuna, outside Uppsala (59°49' N, 17°38' E). This soil was selected because a high degree of preferential flow could be expected (Messing & Jarvis, 1993). The microlysimeters were irrigated four times with filtered rainwater in the laboratory (17.1, 11.8, 18.6 and 18.8 mm). The first irrigation lasted three hours and the following three each lasted two and a half hours. Potassium chloride was applied before the third and fourth irrigations at 74.8 and 81.8 g Cl m⁻² respectively. High time-resolution measurements of percolation and effluent concentrations and resident chloride concentrations at the end of the experiment were made and subsequently used for model testing and parameter identification. This parameter identification study is further described in Paper I.

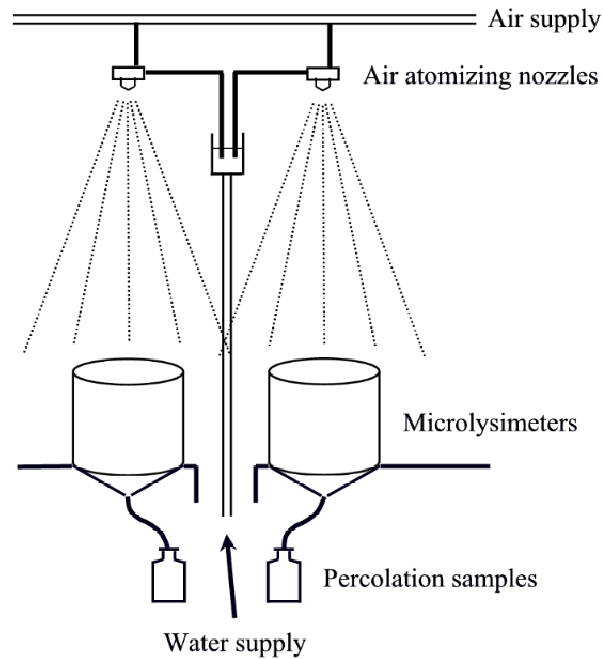


Figure 6. The laboratory setup. Air atomising nozzles placed directly above the microlysimeters create a fine mist, which retains the structure of the soil surface throughout the experiment.

GLUE was applied to the data for parameter identification because it is straightforward and the large number of runs needed for reliable results was not considered a problem for this type of simulation. Four key parameters regulating the degree of preferential flow, the saturated micropore hydraulic conductivity (K_b), the macroporosity ($\theta_{\text{mac,sat}}$), the kinematic exponent in the macropores (n^*) and the diffusion pathlength (d), were included in the parameter identification exercise. The prior uncertainty domains for these parameters were based on expert judgement and preliminary measurements. Tension infiltrometers could preferably be used to directly measure K_b (Messing and Jarvis, 1993). However, the spatial variability of the hydraulic conductivity is often large and measurements cannot be made at the exact location of the microlysimeter sampling since preparation of the infiltration surface will disturb the sample. Therefore, direct measurements can only give approximations of K_b . The impossibility of directly measuring the diffusion pathlength (see *Exchange between pore domains*) justifies a large prior uncertainty. In order to sample these parameters from distributions that are consistent with model responses to changes in parameter values, d and K_b were transformed to d^{-2} and $\log(K_b)$ respectively. All four parameters were then sampled from uniform distributions. The remaining parameters were fixed at values derived from measured data or set to model default values. The equally weighted, additive form of the model efficiency (Eq. [6] and [7]) was used as likelihood function. Twenty thousand simulations were run and corresponding EF values were

calculated. All parameter sets resulting in EF values larger than 0.5 were considered acceptable.

Artificial microlysimeter experiments

Numerical data representing microlysimeter tracer experiments on two hypothetical soils representing one typical clay and one typical loam were generated to further study parameter identification in the MACRO model (Paper II). Prior parameter distributions were chosen to reflect the uncertainty attained after appropriate laboratory and field measurements are conducted. Two mm of irrigation with a concentration of 2.0 kg m^{-3} of a non-reactive tracer was applied on day 1 during two hours ($= 4.0 \text{ g m}^{-2}$). A total of twelve irrigations with zero concentration were then applied with a three-day interval. A cycle of three irrigations of 12, 8, and 4 mm during one hour respectively was repeated four times (equivalent to *ca.* 1 pore volume). The potential evaporation was set to 1 mm d^{-1} to reflect laboratory conditions. ‘Measurements’ were made with ten minutes intervals from the start of each irrigation until the percolation ceased.

Two plausible experimental setups were examined using the model outputs, (i) percolation rate (mm h^{-1}), solute concentration in the effluent water (g m^{-3}) and high time-resolution resident solute concentrations (g m^{-3}) at six depths, hereafter referred to as *all data*, and (ii) measurements of percolation rate, effluent concentration, and one resident solute concentration profile (six depths) at the end of the experiment, hereafter referred to as *limited data*. Only the percolation rate from the first cycle was used in the analysis since the pattern for all four irrigation cycles was identical.

A sensitivity analysis for MACRO has been carried out for pesticide losses from agricultural fields by Dubus & Brown (2002). Since results of a sensitivity analysis tend to depend on the site and scenario considered (Ferreira *et al.*, 1995), a limited sensitivity analysis was performed for this experimental setup. The Morris method was chosen because it is able to examine model sensitivity over entire uncertainty intervals and because of its relatively small computational demand. Each parameter uncertainty interval was divided into 100 equally large layers and Δx_p (see Eq. [14]) was set to 1% of the parameter uncertainty interval. Using a fraction of the parameter uncertainty interval scales the elementary effects to the parameter uncertainty. The elementary effects thereby give information on the reduction in estimation uncertainty that can be expected from a reduction in the parameter uncertainty. The elementary effects were also divided by the value of the corresponding output to enable a comparison between different data groups.

PIMLI was applied to the numerically generated data in order to find an improved measurement scheme for laboratory microlysimeter experiments and to test the possibilities of parameter identification in MACRO. The interval for acceptable parameter sets was arbitrarily set to $\pm 20\%$ of the true value for all types of data. Two thousand five hundred simulations were run in each iteration with parameter sets sampled from the updated distributions. Information contents were calculated for all measurements. The distributions of the accepted parameter values for the ten measurements with largest IC:s were added to make up the posterior

parameter distributions. Parameter sets for the next iteration were created by first dividing each parameter interval into fifteen equally large layers. Each layer was then randomly sampled in proportion to its frequency of accepted parameter values. The parameter value was sampled randomly within the layer. The procedure was stopped after ten iterations since the tenth iteration resulted in only minor reductions in parameter uncertainty.

The decrease in parameter uncertainty (precision) and the location of the posterior mean value in relation to the true value (accuracy) give information on the success of the parameter identification exercise. The precision was evaluated by the reduction coefficient, defined as one minus the posterior standard deviation divided by the prior standard deviation. The distance, given in standard deviations of the posterior distribution, between the true value and the mean value of the posterior distribution was used as a measure of accuracy. Ideally, the mean value of the (normally distributed) posterior distribution should equal the true value.

The field data set

An experiment carried out on a well-structured silty clay (defined as a Typic Eutrochrept, USDA) at Lanna in Västergötland, Sweden (58°21' N, 13°08' E) was used for the parameter identification study using field data (Paper III). The data set was selected because it is comprehensive and because it shows strong evidence of a high degree of preferential flow (Larsson & Jarvis, 1999). Tile-drains are installed at 1-m depth at 13.5-m spacing, draining a plot 0.4 ha in size. Bentazone (2.51 kg ha⁻¹) and potassium bromide (44.4 kg Br ha⁻¹) were simultaneously applied in the autumn of 1994. Apart from standard measurements of soil physical and hydraulic properties, the data from Lanna consist of daily measurements of drainflow during more than one year, concentrations of bentazone and chloride in drainflow sampled every 1.5 mm of drainflow, resident concentrations at five depths on three occasions for bentazone and five occasions for bromide, and water content measured at nine depths on five occasions.

MACRO was parameterised for the Lanna field based on the data of soil physical and hydraulic properties (Larsson & Jarvis, 1999). Where data did not exist, parameters were determined by: (i) inbuilt pedotransfer functions (van Genuchten/Mualem model parameters for the subsoil), (ii) recommendations by Forum for the Coordination and Use of Pesticide Fate Models and Their Use (2000) (Freundlich exponent and the diffusion coefficient for bentazone in free water), and (iii) model default values.

Six key parameters were investigated using SUFI and GLUE. The parameters were chosen either because they are difficult to estimate through direct measurements or because they were considered sensitive based on prior experience with the model (Dubus & Brown, 2002). All parameters were assigned uniform distributions within their uncertainty limits in accordance with Beven & Binley (1992). It should be noted that many of the parameters not included in the calibration are to some extent uncertain and sensitive. However, to limit the computational work only the most sensitive parameters could be included.

The model efficiency assuming equal weights was used for both the SUFI calibration and the GLUE analysis. The critical tolerance in SUFI, as well as the limit defining acceptable simulations in GLUE was defined in absolute terms as the maximum EF_{tot} value, $EF_{tot,max}$, minus 0.2. In SUFI, all strata with zero hits at the critical tolerance were removed between iterations. The iterations stopped when no further reduction was possible at the critical tolerance. Following Roulier & Jarvis (2003a), SUFI was first applied to parameters controlling the degree of macropore flow against data of water content, drainflow and resident and flux concentrations of bromide. In a second step, pesticide properties were calibrated on the bentazone data, retaining the parameter values from the first calibration step. In GLUE, thirty thousand simulations with parameter values generated using Latin hypercube sampling, were run both for bromide and for bentazone.

GLUE was also used for evaluating the effects of data availability on parameter conditioning since model efficiencies calculated for each group of data can easily be combined. The groups of data were combined in four different ways, (i) all observations (*All*), (ii) only soil water contents and resident concentrations of bromide and bentazone (*Res*), (iii) only drainflow and flux concentrations of bromide and bentazone (*Flux*) and (iv) soil water contents, drainflow and both resident and flux concentrations of bentazone (*NoTracer*). In this study, all parameter sets with corresponding EF_{tot} values within 0.2 of $EF_{tot,max}$ were considered acceptable. This definition of the threshold allows comparison of parameter conditioning between groups of data with different $EF_{tot,max}$ values.

The experiments at Lanna did not reflect normal agricultural practice since bentazone was applied on bare soil in autumn at a dose much higher than recommended. The posterior uncertainty intervals from SUFI and the posterior likelihood distributions from GLUE were therefore used to predict the accumulated leaching and the maximum concentration in drainflow for a scenario applying good agricultural practice. The model was re-parameterised for spring application of bentazone at the maximum recommended dose (1.305 kg ha^{-1}). The crop parameters, taken from Forum for the Coordination of Pesticide Fate Models and Their Use (2001), were chosen to represent field peas (*Pisum sativum*, L). The same driving data as in the calibration was used. SUFI does not provide information on the distribution of parameter values within the posterior uncertainty domains. Therefore, parameters sets were generated using Latin hypercube sampling from uniform distributions. Since all prior distributions were uniform, GLUE posterior distributions are simply given by normalising the likelihood distribution. The effect of data availability on predictions was tested, using the same groups as in the analysis of parameter conditioning.

Results and discussion

Model development

The improved numerical solutions in MACRO 5.1 were successfully verified by comparisons between simulation results and analytical solutions for a variety of water flow and solute transport problems in Vanderborght *et al.* (2005) and Paper I. Depending on the type of application, run times were reduced by 50 to 90% compared to the previous version of MACRO.

The infiltration rate into the micropores of an initially dry soil is shown in Fig. 7a for nodal distances of 0.5 and 5.0 cm. The larger nodal distance results in larger infiltration, which is in accordance with results reported by van Dam (2000). Fig. 7b shows the solute infiltration rate into macropores for the two nodal distances. Solutes stored within the mixing depth in the micropores enter the macropores when macropore infiltration starts. Solute infiltration into the macropores decreases as the solutes in the mixing depth are depleted. The larger nodal distance results in a retardation of the solute infiltration and a smaller maximum value. The effects of smaller nodal distances on pesticide leaching in field applications are difficult to assess since model error, errors in parameter values and uncertainty in input data might have a larger impact on the accuracy of model simulations. However, the improved numerical accuracy compared to previous versions of the model eliminates one source of uncertainty, thus improving the chances of finding ways to reduce others.

A comparison between simulations with MACRO 5.1 and the previous version of MACRO would be interesting but probably difficult to interpret. Differences originating from changes in model concepts could probably not be separated from changes due to improved numerical solutions. Therefore, such a comparison is not included in this thesis.

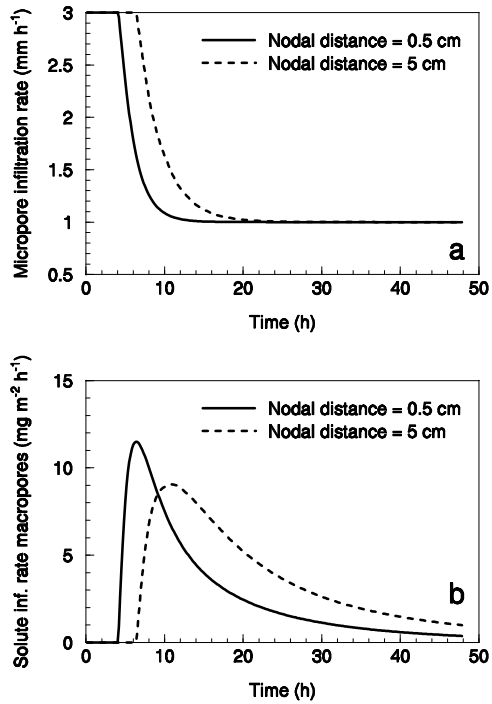


Fig. 7. Effects of different nodal distances for infiltration into a dry clay soil, a) micropore infiltration, and b) solute infiltration into macropores.

The laboratory microlysimeter experiment

MACRO 5.1 could accurately simulate the high-resolution tracer data from the microlysimeter experiments (EF values of 0.64, 0.48 and 0.74 for percolation rate, solute leaching rate and resident solute concentration respectively). The measured solute leaching rate, indicative of strong preferential flow, is shown in Fig. 8 together with the best GLUE simulation and the maximum and minimum values using all simulations with EF values larger than 0.5. The leaching pattern was excellently captured.

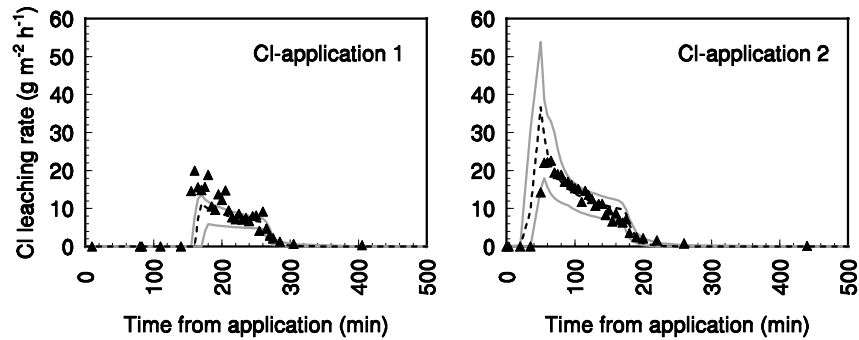


Fig. 8. Solute leaching rates from the laboratory microlysimeter experiment following solute applications. The best GLUE simulation (black dotted line) and the minimum and maximum values of the simulations with EF values larger than 0.5 (grey lines) are compared to measurements (triangles).

The results from the parameter identification exercise using GLUE are summarised in Table 2. The posterior uncertainty, defined by the 5th and the 95th percentiles for the accepted parameter sets was reduced by more than 80% for the diffusion pathlength. This large reduction of the uncertainty is related to the relatively large prior uncertainty. Due to the difficulties in deriving prior information for the diffusion pathlength a large prior uncertainty is usually needed. The kinematic exponent for the macropores (n^*) was poorly constrained by the measurements even though the prior uncertainty domain was thought to include all feasible values. Problems with simultaneous identification of the macroporosity ($\theta_{\text{mac,sat}}$) and n^* could be expected since they are intimately related through Eq. [9]. Both the saturated micropore hydraulic conductivity (K_b) and $\theta_{\text{mac,sat}}$ were, at least to some extent, constrained by the data.

Table 2. Prior and posterior parameter uncertainty for the laboratory microlysimeter experiment. The 5th and 95th percentiles are used to define the posterior uncertainty.

| Parameter | Prior uncertainty | Posterior uncertainty |
|---|-------------------|-----------------------|
| Saturated micropore hydraulic conductivity (mm h^{-1}) | 0.1–10 | 0.16–4.9 |
| Macroporosity (%) | 1.5–4.5 | 2.4–3.8 |
| Kinematic exponent, macropores (-) | 2–8 | 2.2–7.4 |
| Diffusion pathlength (mm) | 2.5–50 | 6.0–15 |

Artificial microlysimeter experiments

Average elementary effects from the Morris sensitivity analysis of twelve parameters in MACRO 5.1 using *all data* for time series of percolation and both resident and effluent concentrations are shown in Fig. 9 for the hypothetical clay and loam soils. The most sensitive parameters were d , $\theta_{\text{mac,sat}}$, K_b and the

dispersivity (D_v) for both soils. The diffusion pathlength was mainly sensitive to the effluent concentration and the resident concentration, $\theta_{\text{mac,sat}}$ to the percolation rate and the effluent concentration whereas K_b and D_v were mainly sensitive to the effluent and resident concentration. For the loam, α was also sensitive, mainly to the percolation rate. The higher sensitivity of d for the loam is probably due to a larger uncertainty interval, which also included small values where the sensitivity is high.

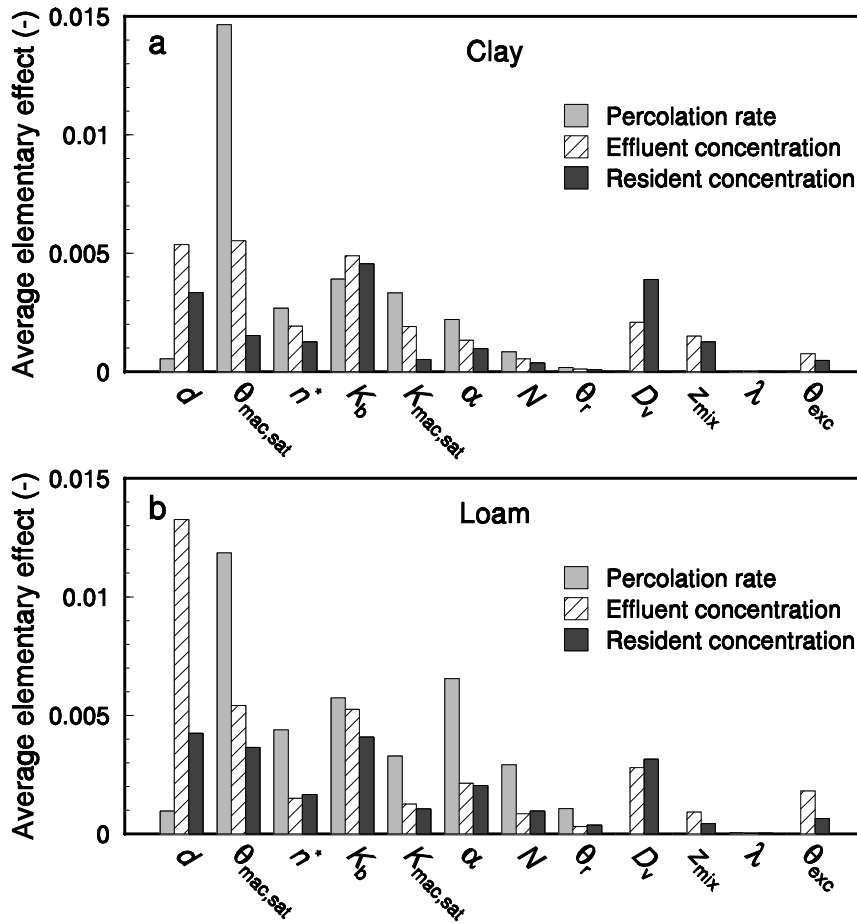


Fig. 9. Morris sensitivity analysis results showing average elementary effects due to a change in a parameter value of 1% of the parameter uncertainty interval for, a) hypothetical clay and b) hypothetical loam. The elementary effects for resident concentration are average values for six depths. High time-resolution measurements of resident concentrations were used. The parameters are: d , diffusion pathlength; $\theta_{\text{mac,sat}}$, macroporosity; n^* , kinematic exponent; K_b , saturated micropore hydraulic conductivity; $K_{\text{mac,sat}}$, saturated macropore hydraulic conductivity; α , van Genuchten alpha; N , van Genuchten N; θ_r , residual water content; D_v , dispersivity; z_{mix} , mixing depth; λ , micropore tortuosity factor; θ_{exc} , excluded water due to anion exclusion.

The results from the PIMLI exercise are summarised in Table 3 for the hypothetical clay and in Table 4 for the hypothetical loam. For the clay, uncertainties were reduced by more than 50% for six parameters using *all data*. The prior distributions for the remaining parameters were left unaltered or only slightly changed by the process. These parameters were also least sensitive according to the Morris analysis (Fig. 9a and b). The true values of d , n^* , K_b and D_v were within one standard deviation of the posterior mean value, indicating that the posterior distributions of these parameters converged towards their true values during the iterative process. The mean value for $K_{\text{mac,sat}}$ was smaller than the true value. The underestimation of $K_{\text{mac,sat}}$ was probably compensated by an underestimation of $\theta_{\text{mac,sat}}$.

Uncertainties were reduced in eight parameters for the hypothetical loam using *all data* (Table 4). In addition to the parameters for which the uncertainty was reduced for the clay, also the uncertainty for θ_{exc} was reduced. This is in accordance with the Morris analysis, which showed that this parameter was more sensitive for the loam (Fig. 9a and b). The macroporosity was also successfully identified. Even though n^* was identified both accurately and with high precision, it was evident from a visual inspection of the histograms of its posterior distribution, that it converged towards the lower limit of its uncertainty interval.

Table 3. Results from the PIMLI analysis for the hypothetical clay soil. The table shows true values, mean values and standard deviations (in parenthesis) for the posterior distributions after ten iterations, and reduction coefficients defined as one minus the posterior standard deviation divided by the prior standard deviation.

| Parameter† | True value | Posterior | | Reduction coefficient | |
|---------------------------|------------|-----------------|---------------------|-----------------------|-----------------|
| | | <i>All data</i> | <i>Limited data</i> | <i>All data</i> | <i>Ltd data</i> |
| d | 20 | 20.5*(3.66) | 19.9*(3.25) | 0.72 | 0.75 |
| $\theta_{\text{mac,sat}}$ | 3.0 | 2.71(0.19) | 2.90*(0.24) | 0.86 | 0.82 |
| n^* (-) | 3.0 | 3.16*(0.27) | 2.99*(0.25) | 0.81 | 0.83 |
| K_b | 1.0 | 1.05*(0.16) | 1.09*(0.19) | 0.69 | 0.65 |
| $K_{\text{mac,sat}}$ | 50 | 37.0(8.3) | 37.9(8.07) | 0.57 | 0.58 |
| α | 0.02 | 0.020*(0.010) | 0.021*(0.011) | 0.09 | 0 |
| N | 1.1 | 1.09*(0.030) | 1.09*(0.030) | 0 | 0 |
| θ_r | 5.0 | 5.0*(1.9) | 5.0*(1.9) | 0 | 0 |
| D_v | 3.0 | 2.90*(0.24) | 3.0*(1.15) | 0.80 | 0 |
| z_{mix} | 1.0 | 1.75(0.72) | 1.75(0.72) | 0 | 0 |
| λ | 0.5 | 0.5*(0.29) | 0.5*(0.29) | 0 | 0 |
| θ_{exc} | 5.0 | 5.0*(2.89) | 5.0*(2.89) | 0 | 0 |

* The true value is within one standard deviation.

† d (mm), diffusion pathlength; $\theta_{\text{mac,sat}}$ (%), macroporosity; n^* (-), kinematic exponent; K_b (mm h^{-1}), saturated micropore hydraulic conductivity; $K_{\text{mac,sat}}$ (mm h^{-1}), saturated macropore hydraulic conductivity; α (-), van Genuchten alfa; N (-), van Genuchten N; θ_r (%), residual water content; D_v (cm), dispersivity; z_{mix} (mm), mixing depth; λ (-), micropore tortuosity factor; θ_{exc} (%), excluded water due to anion exclusion.

Table 4. Results from the PIMLI analysis for the hypothetical loam soil. The table shows true values, mean values and standard deviations (in parenthesis) for the posterior distributions after ten iterations, and reduction coefficients defined as one minus the posterior standard deviation divided by the prior standard deviation.

| Parameter† | True value | Posterior | | Reduction coefficient | |
|---------------------------|------------|----------------|---------------|-----------------------|----------|
| | | All data | Limited data | All data | Ltd data |
| d | 5 | 5.12*(0.61) | 4.85*(0.48) | 0.96 | 0.97 |
| $\theta_{\text{mac,sat}}$ | 3.0 | 3.07*(0.42) | 3.28*(0.31) | 0.68 | 0.77 |
| n^* (-) | 3.0 | 2.72*(0.53) | 2.23(0.17) | 0.63 | 0.88 |
| K_b | 3.0 | 2.81*(0.53) | 1.25(0.22) | 0.61 | 0.84 |
| $K_{\text{mac,sat}}$ | 50 | 40.8*(15.1) | 26.0(5.45) | 0.22 | 0.72 |
| α | 0.05 | 0.043*(0.0086) | 0.036(0.0054) | 0.41 | 0.63 |
| N | 1.5 | 1.50*(0.088) | 1.50*(0.088) | 0 | 0 |
| θ_r | 5.0 | 5.0*(1.9) | 5.0*(1.9) | 0 | 0 |
| D_v | 3.0 | 3.05*(0.20) | 3.0*(1.15) | 0.83 | 0 |
| z_{mix} | 1.0 | 1.75(0.72) | 1.75(0.72) | 0 | 0 |
| λ | 0.5 | 0.5*(0.29) | 0.5*(0.29) | 0 | 0 |
| θ_{exc} | 5.0 | 3.96*(2.47) | 2.61(1.81) | 0.14 | 0.37 |

* The true value is within one standard deviation.

† d (mm), diffusion pathlength; $\theta_{\text{mac,sat}}$ (%), macroporosity; n^* (-), kinematic exponent; K_b (mm h^{-1}), saturated micropore hydraulic conductivity; $K_{\text{mac,sat}}$ (mm h^{-1}), saturated macropore hydraulic conductivity; α (-), van Genuchten alfa; N (-), van Genuchten N; θ_r (%), residual water content; D_v (cm), dispersivity; z_{mix} (mm), mixing depth; λ (-), micropore tortuosity factor; θ_{exc} (%), excluded water due to anion exclusion.

When only *limited data* were used, the process did not reduce the uncertainty in D_v independent of soil type. The posterior distributions of the other parameters were generally similar to those obtained using *all data* except for K_b , n^* and $K_{\text{mac,sat}}$ which had larger reduction coefficients and converged towards even smaller (and incorrect) values for the loam. The failure to constrain D_v did not have a large effect on the posterior distributions of the other parameters but might be important for the identification of sorption and transformation parameters in simulations with reactive solutes.

In all cases, measurements with large information content were generally found during the first irrigation cycle. For successful identification of d , $\theta_{\text{mac,sat}}$ and K_b , the peak outflows and the concentrations in the recession phases must be captured. This indicates that high time-resolution measurements during the first irrigations following application will result in data containing more information for parameter identification than low time-resolution data obtained from a larger number of irrigations.

The field data set

MACRO could fairly well simulate observations of soil water contents, drainflow, both resident and effluent concentrations of bromide and bentazone from the Lanna field site (Table 5). Visual comparisons are presented in Paper III. The largest EF values for individual groups were in most cases much larger than the corresponding

EF value obtained from the best overall simulation obtained with GLUE. This is generally the case for multi-criteria problems (Gupta, Sorooshian & Yapo, 1998) and reflects errors in model process descriptions, parameterisation and measurements. Comprehensive data sets, such as Lanna, are needed to highlight these problems.

Table 5. Model efficiencies (EF) for simulations using the optimal sequential uncertainty domain parameter fitting (SUFI) parameter values, the best generalized uncertainty estimation (GLUE) parameter set and the optimal GLUE parameter set for each group.

| Group | SUFI | GLUE | Optimal |
|-----------------------------------|---------|--------|---------|
| Soil water contents | 0.483 | 0.512 | 0.539 |
| Drainflow | 0.258 | 0.300 | 0.437 |
| Resident bromide concentrations | 0.215 | 0.340 | 0.797 |
| Flux bromide concentration | 0.164 | -0.199 | 0.327 |
| Resident bentazone concentrations | 0.802 | 0.688 | 0.816 |
| Flux bentazone concentrations | -0.0751 | -0.194 | 0.312 |
| All groups (=EF _{tot}) | 0.308 | 0.241 | - |

The SUFI procedure reduced all initial uncertainty domains except for d in the subsoil (Table 6). However, many GLUE simulations with parameter values lying outside the SUFI posterior uncertainty domains had EF values larger than the threshold (Paper III), indicating that the uncertainty domains were sometimes reduced too much. Many parameter sets sampled from within the posterior uncertainty domains resulted in poor simulations with the minimum EF value being -3.2 . This is probably because SUFI did not determine the posterior uncertainty domains correctly in all cases and does not account for parameter correlations.

Table 6. Initial and final uncertainty domains for SUFI and optimal parameter values obtained from both the SUFI and GLUE procedures.

| Parameter† | Initial uncertainty domain | Posterior uncertainty domain | Optimal SUFI parameter value | Parameter value for best GLUE simulation |
|---|----------------------------|------------------------------|------------------------------|--|
| K_b , 1–175 cm, (mm/h) | 0–0.25 | 0.0833–0.167 | 0.104 | 0.119 |
| d_{top} (mm) | 0–300 | 50–300 | 70.8 | 61.5 |
| d_{sub} (mm) | 0–300 | 0–300 | 75.0 | 82.4 |
| K_{oc} (cm ³ g ⁻¹) | 0–16 | 0–2.67 | 0.222 | 1.83 |
| μ_{top} (d ⁻¹) | 0–0.25 | 0.0556–0.125 | 0.0845 | 0.0708 |
| μ_{sub} (d ⁻¹) | 0–0.25 | 0–0.0833 | 0.0208 | 0.0309 |

† K_b , saturated micropore hydraulic conductivity; d , diffusion pathlength; K_{oc} , organic carbon partition coefficient; μ , degradation rate coefficient. The subscripts top and sub denote topsoil and subsoil respectively.

The results from the GLUE analysis using different groups of data for parameter conditioning are presented in Fig. 10. Using *All* gave the highest degree of parameter conditioning. However, not all parameters were highly conditioned even with such a comprehensive data set as *Lanna*. The diffusion pathlength in the topsoil was especially difficult to identify. The highly irregular pattern of the hourly rainfall used as driving data results in different flow rates in the macropores. The different time scales for equilibration between pore domains are likely to reduce the possibilities to identify the diffusion pathlength (see *Exchange between pore domains*), which may have contributed to the poor conditioning in the topsoil. The parameters were generally poorly conditioned by *Res*. This is not surprising for K_b and d_{sub} considering the low sensitivity of these macropore flow parameters to this type of measurement. The failure to condition K_d and μ_{sub} is probably due to infrequent sampling in time and large spatial variability of these field measurements (Larsson & Jarvis, 1999). A high degree of conditioning was attained using *NoTracer* for all parameters except K_{oc} and d_{top} . Differences in parameter conditioning between *All* and *NoTracer* show that tracer data contain information on solute transport that is not included in the bentazone data. This indicates that parameter correlations can lead to incorrect estimates when tracer data are lacking.

Random sampling of the SUFI posterior uncertainty domains resulted in larger prediction uncertainty compared to GLUE (table 7). This is because the SUFI posterior uncertainty domains contain parameter combinations that are poor simulators due mainly to parameter correlations. Table 7 shows that *All* and *NoTracer* resulted in the smallest prediction uncertainty ranges.

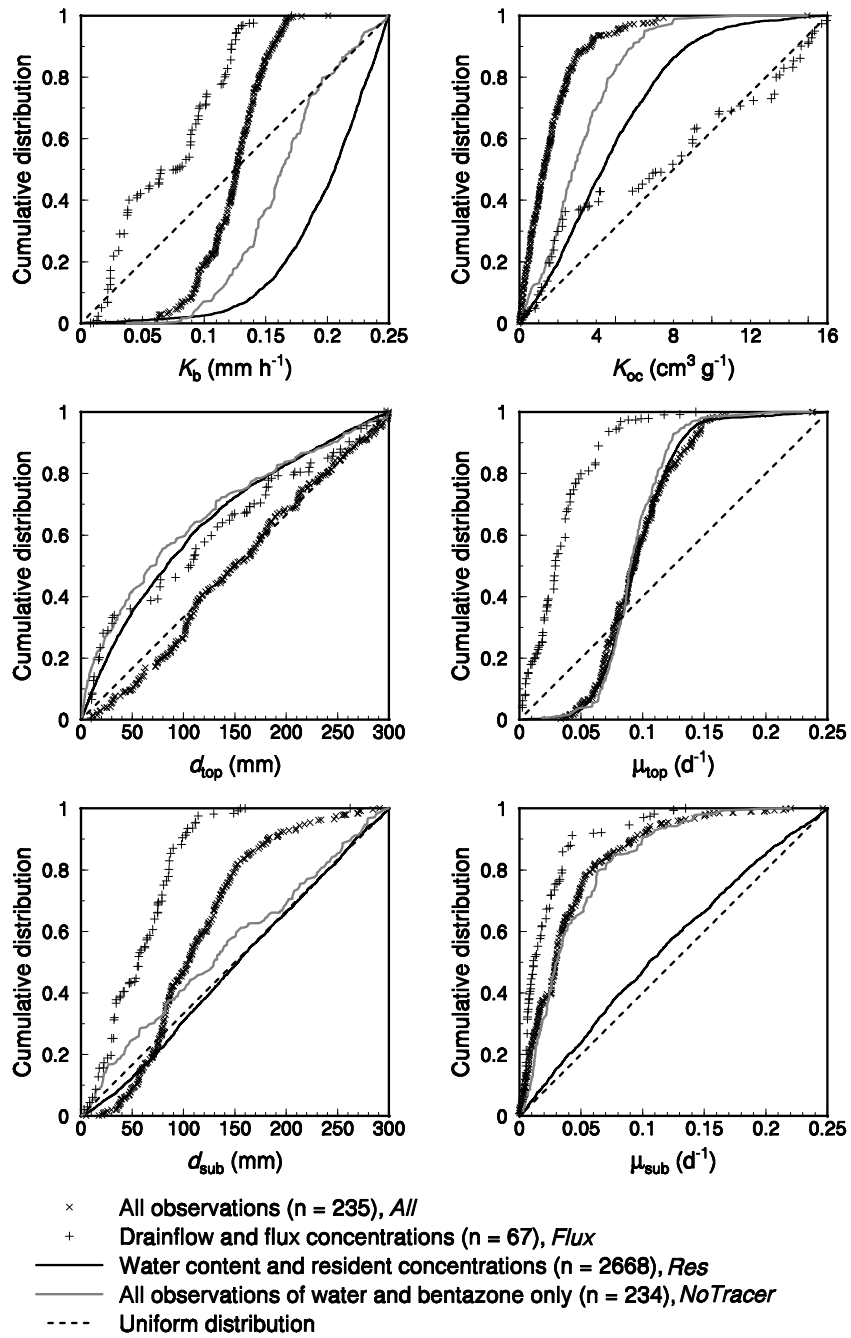


Fig 10. Cumulative likelihood distributions for parameter conditioning with generalised likelihood uncertainty estimation (GLUE) using different combinations of observations. The number of acceptable simulations included in each combination of groups is denoted n . The term K_b is the saturated matrix hydraulic conductivity, K_{oc} is the organic carbon partition coefficient, d is the diffusion pathlength and μ is the degradation rate coefficient. The subscripts top and sub denote topsoil and subsoil respectively.

Table 7. Results from the predictive simulations for SUFI and GLUE using different combinations of observations.

| | Maximum bentazone concentration in drainflow | | | Accumulated losses of bentazone through drains | | |
|----------|--|-----------------------------|-----------------------------|--|-----------------------------|-----------------------------|
| | 5 th percentile | 50 th percentile | 95 th percentile | 5 th percentile | 50 th percentile | 95 th percentile |
| | mg m ⁻³ | | | [%] | | |
| SUFI | 37.4 | 76.0 | 279 | 2.03 | 4.99 | 22.4 |
| All | 40.9 | 95.2 | 198 | 2.56 | 7.19 | 18.7 |
| Res | 45.2 | 139 | 383 | 1.24 | 6.47 | 23.5 |
| Flux | 67.1 | 155 | 316 | 5.37 | 11.7 | 21.2 |
| NoTracer | 79.7 | 142 | 237 | 4.58 | 8.59 | 17.1 |

Conclusions

The use of implicit numerical solutions for water flow, solute transport and heat flow in the improved version of the MACRO model reduces run times significantly compared to explicit solutions even when a much finer spatial discretisation is used in the implicit schemes. Reasonably short run-times are a prerequisite for successful parameter identification using inverse modelling. The improved model could accurately simulate high time-resolution measurements of percolation rate, leaching rate and resident chloride concentrations from laboratory microlysimeter experiments showing a high degree of preferential flow. Data of soil water contents, drainflow and flux and resident concentrations of bentazone and bromide from a field experiment on a structured clay soil were fairly well simulated.

Data from laboratory microlysimeter experiments contained enough information to reduce the prior uncertainty of the parameter describing mass exchange between pore domains, the saturated matrix hydraulic conductivity and the macroporosity. Simultaneous identification of the macroporosity, the macropore hydraulic conductivity and the kinematic exponent was not possible, probably because of parameter correlations. Using numerically generated data representing one clay and one loam soil it was shown that high time-resolution measurements of resident concentrations were needed to reduce the uncertainty in the dispersivity (dispersion length) and to avoid biased estimates of the saturated micropore and macropore hydraulic conductivities for the loam.

Measurements with large information content for parameter identification were found during the first irrigations after solute application for the hypothetical soils. Data on peak outflows and effluent concentrations at the end of recession phases contained most information for identification of the parameter describing mass exchange between pore domains, the saturated matrix hydraulic conductivity and the macroporosity. This indicates that high time-resolution measurements during

the first irrigations following application will provide more information than low time-resolution data from a larger number of irrigations.

All groups of data from the field experiment were needed to get highly conditioned and unbiased parameter estimates using GLUE. However, the parameter describing mass exchange between pore domains was poorly conditioned even with a very comprehensive data set. SUFI decreased the initial uncertainty domains significantly for all parameters except for the diffusion pathlength in the subsoil. However, random sampling from SUFI posterior uncertainty domains resulted in larger prediction uncertainty compared to GLUE. This is because these domains contain parameter combinations that are poor simulators due mainly to parameter correlations.

Future research and recommendations

We must keep in mind the goals of modelling, which may be to increase our understanding of the system that we simulate, or, to make as accurate predictions as possible. When the goal is to make predictions it is of limited use to ensure that a calibration problem is well-posed by reducing the number of parameters. Calibrated values will be dependent on the assumed values of the parameters not included and the bias in parameter values might have consequences for model predictions when the setting is changed, for example from the lysimeter scale to the field scale, or when the precipitation pattern changes. By reducing the number of calibrated parameters we are saying that the model is overparameterised, not only for the experiment used for optimisation, but for all cases where the calibrated parameter distributions are used. This might of course be the case, but it certainly needs to be proven before accepted. Hence, the best way to deal with equifinality is to accept it.

Although there has been great progress in preferential flow modelling during the last two decades there are still problems that need to be resolved to increase confidence in modelling results. Model descriptions can certainly be improved but an increase of model complexity will be of limited use as long as the uncertainty in parameterisation is large. Therefore, parameter identification remains one of the greatest challenges in this area of research. Data from tracer microlysimeter experiments can be used to reduce the uncertainty in parameters determining the degree of preferential flow. However, the applicability of these parameters especially for field conditions should not be taken for granted. The simplifications in the first-order mass transfer approach require that the effects of changing both spatial and temporal scales are examined before calibrated values are used for predictions.

We have seen that probabilistic approaches generated new knowledge about the possibilities and limitations of parameter identification in dual-permeability models for water flow and solute transport. Although it is not possible to objectively determine the posterior parameter probability distributions, these methods can be

used to study effects of data availability on the uncertainty in parameterisation and predictions and to evaluate for which parameters a reduction of the uncertainty will be critical. The search for unique 'optimal' parameter values in dual-permeability models should be abandoned in favour of probabilistic approaches.

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