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A review of model applications for structured soils: b) Pesticide transport

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ABSTRACT

The past decade has seen considerable progress in the development of models simulating pesticide transport in structured soils subject to preferential flow (PF). Most PF pesticide transport models are based on the two-region concept and usually assume one (vertical) dimensional flow and transport. Stochastic parameter sets are sometimes used to account for the effects of spatial variability at the field scale. In the past decade, PF pesticide models were also coupled with Geographical Information Systems (GIS) and groundwater flow models for application at the catchment and larger regional scales. A review of PF pesticide model applications reveals that the principal difficulty of their application is still the appropriate parameterization of PF and pesticide processes. Experimental solution strategies involve improving measurement techniques and experimental designs. Model strategies aim at enhancing process descriptions, studying parameter sensitivity, uncertainty, inverse parameter identification, model calibration, and effects of spatial variability, as well as generating model emulators and databases. Model comparison studies demonstrated that, after calibration, PF pesticide models clearly outperform chromatographic models for structured soils. Considering nonlinear and kinetic sorption reactions further enhanced the pesticide transport description. However, inverse techniques combined with typically available experimental data are often limited in their ability to simultaneously identify parameters for describing PF, sorption, degradation and other processes. On the other hand, the predictive capacity of uncalibrated PF pesticide models currently allows at best an approximate (order-of-magnitude) estimation of concentrations. Moreover, models should target the entire soil–plant–atmosphere system, including often neglected above-ground processes such as pesticide volatilization, interception, sorption to plant residues, root uptake, and losses by runoff. The conclusions compile progress, problems, and future research choices for modelling pesticide displacement in structured soils.

1. Introduction

As a result of agricultural practices, pesticides have been detected in many aquifers and surface waters. In structured soils, macropore flow often causes rapid nonuniform leaching via preferential flow paths, where a fraction of the contaminant percolates into ground water before it can degrade or be adsorbed by the soil (e.g., Stagnitti et al., 1994). With regard to pesticides, moderately sorbed compounds with relatively short half-lives are particularly affected (Larsson and Jarvis, 2000). Travel times for pesticides preferentially leached below the root zone are comparable to those for conservative solutes, with losses of typically less than 1% of the

Abbreviations: 1D, One-Dimensional; 2D, Two-Dimensional; 3D, Three-Dimensional; BC, Boundary Conditions; BTC, Break Through Curve; CDE, Convection-Dispersion Equation; CNE, Chemical Non-Equilibrium; DFM, Discrete Fracture Model; DPM, Dual-Permeability Model; ET, evapotranspiration; GIS, Graphical Geographic System; IC, Initial Conditions; K_D, Sorption distribution coefficient; K_{OC}, Sorption distribution coefficient normalized to organic carbon; KW, Kinematic Wave; m, soil matrix; MIM, Mobile-Immobile Water Content Model; MRM, multireaction model; PF, Preferential Flow; PNE, Physical Non-Equilibrium; SOM, soil organic matter; SPM, Single-Porosity Model; T, temperature; θ, soil moisture content.

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applied dose, but reaching up to 5% of the applied mass (Flury, 1996; Kladivko et al., 2001; FOCUS, 2001). These apparently small numbers can be put into perspective by considering the EU drinking water standard, which states that concentrations of a single pesticide may not exceed 0.1 μg l^{-1}. For a dose of 0.2 kg ha^{-1} and an annual recharge of 200 mm, this implies a maximum allowed leaching loss of only 0.1% of the applied amount (Jarvis, 2007). Hence, macropore flow should be considered in risk assessment of ground water contamination with pesticides (FOCUS, 2000).

Pesticide leaching through the vadose zone to ground water is a complex process controlled by a range of soil and environmental conditions. Accordingly, pesticide fate models account for a variety of processes including soil water flow, solute transport, heat transport, pesticide sorption, transformation and degradation, volatilization, crop uptake, and surface runoff. A particular modelling challenge is to predict pesticide transport at very low leaching levels important for pesticide registration. These low leaching percentages may be associated with PF, where only a small fraction of the chemical percolates downward at a fast pace, while the remaining bulk of the substance leaches more slowly than would be expected from the chromatographic theory (Boesten, 2000). On the other hand, it has been argued that for very low concentrations, approaching the level of quantification, the criteria for accuracy need not be as rigorous, particularly when the analysis takes into account the uncertainty of data and model outcome (Carbone et al., 2002). An evaluation of model predictive accuracy is often made using the factor-of-*f* approach, where the agreement between model estimates versus measured values is considered satisfactory within two-, five-, and 10-fold differences (Parrish and Smith, 1990). This approach allows the nature of the measured data to serve as an input to set the bounds that define the precision of the model (Carbone et al., 2002).

This contribution reviews recent model applications for evaluating pesticide transport in structured soils, at scales ranging from the soil column to the catchment. We attempt to identify the progress made during the past 10 years, as well as some of the developments still required. This paper complements the overview of model applications of preferential water flow and tracer transport (Köhne et al., 2008-this issue). Since pesticides

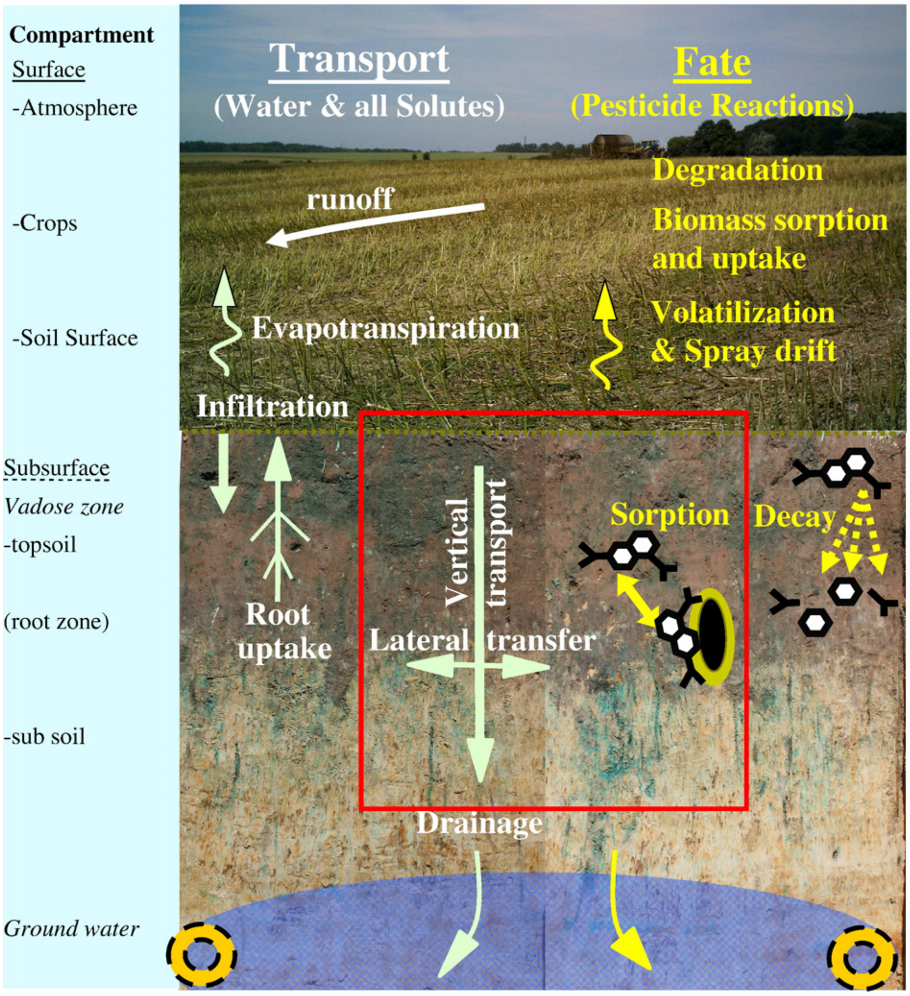

Fig. 1. Principal processes governing pesticide transport and fate in agricultural structured soil systems. The central frame is explained in Fig. 2.

encompass a variety of organic chemicals with a wide range of physico-chemical properties, the conclusions presented in this manuscript are not limited necessarily to pesticides, but may also be relevant to other reactive organic solutes with similar leaching behavior. The paper starts with an overview of reviewed models (Section 2). Model applications are then reported in sections related to particular scales, ranging from the soil column up to the field (Sections 3.1–3.2). Selected applications at larger scales are then reported in Section 4. Strengths and potential weaknesses of models most commonly applied for simulating preferential transport of pesticides at the field scale are discussed in Section 4. Finally, in Section 5 conclusions are drawn about the current state of modelling of preferential pesticide transport and future research needs are proposed.

2. Overview of models for simulating pesticide transport in preferential flow systems

The principal processes governing pesticide transport and fate in agricultural structured soil systems are illustrated in Fig. 1. Soil matrix and macropore characteristics invoking different transport patterns are highlighted in Fig. 2.

Descriptions of models for simulating transport of pesticides (and other chemicals) can be found in several reviews and model comparison studies (e.g., Jarvis, 1998; Armstrong et al., 2000a; Boesten, 2000; Vanclooster et al., 2000a; Beulke et al., 2001a; Garratt et al., 2003; Malone et al., 2004a; Gärdenäs et al., 2006; Ma et al., 2007; Šimůnek and van Genuchten, 2008). In this section, a brief overview of those

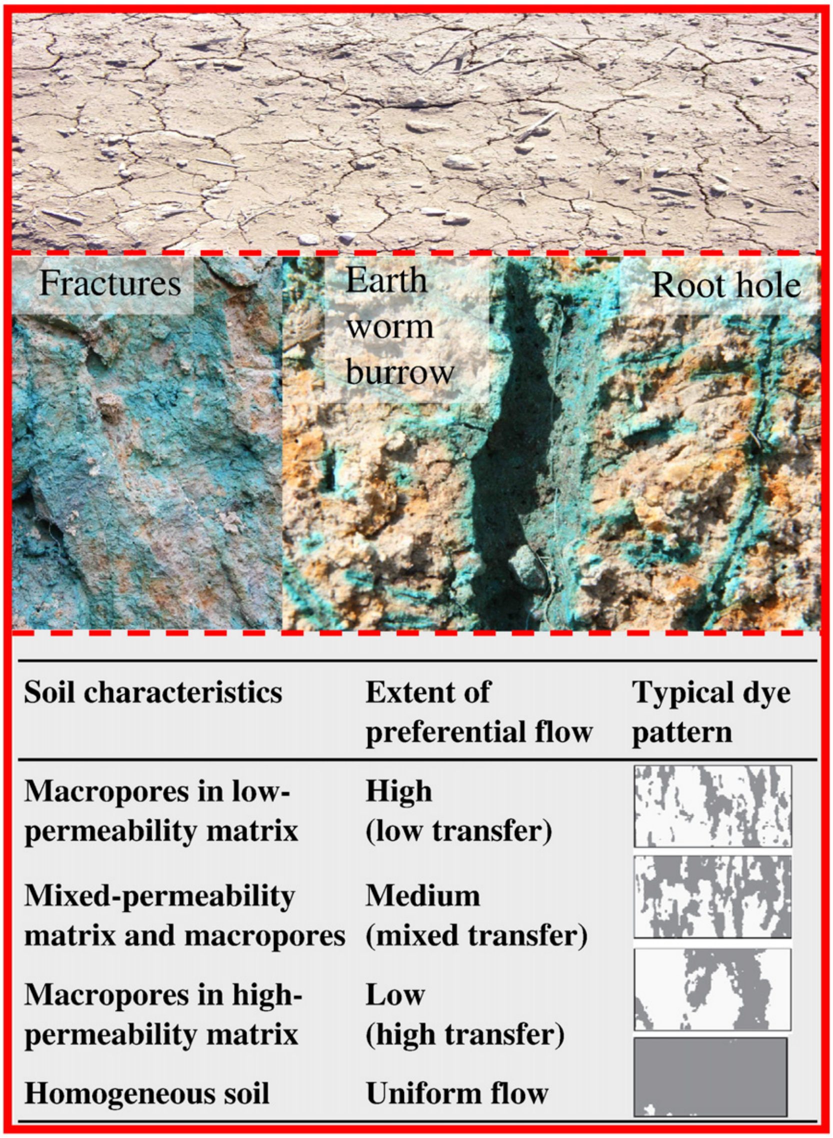

Fig. 2. Fractures and microtopography are triggers for preferential infiltration (top), Diverse structure/matrix interfaces stained by dye tracer visualize different preferential transport paths; these interfaces may affect lateral diffusion, sorption and degradation (middle). Soil matrix and macropore characteristics and resulting transport patterns; actual patterns also depend on the characteristics of rainfall and of overlaying soil horizons (simplified after Weiler and Flühler, 2004) (bottom).

models that account for preferential pesticide transport is given. For the description of models simulating water flow and non-reactive transport, the reader is referred to our companion paper (Köhne et al., 2008-this issue). Main model characteristics additionally relevant for simulating preferential pesticide transport are listed below. Besides physical nonequilibrium (PNE) caused by rate-limited solute transfer between transport regions of different mobility, several models also consider chemical nonequilibrium (CNE) caused by rate-limited sorption. As an example, a model concept of two mobile regions with equilibrium and kinetic sorption is illustrated in Fig. 3. Unless stated otherwise, all models are one-dimensional (1D) and use a numerical solution. Features of some more common models are additionally shown in Table 1.

2.1. Root Zone Water Quality Model (RZWQM)

The RZWQM (Ahuja et al., 2000a,b) is an agricultural systems model that can simulate water flow and agrochemical movement in macroporous soils. The pesticide component supports various reaction processes, such as first-order degradation adjusted for soil water content, temperature, and depth, and sorption in the matrix (but not in the macropores) to equilibrium, kinetic, and irreversibly binding sites. Chemical transfer between macropores and matrix is simulated assuming instant mixing between water in the macropores and in an adjacent thin (e.g., 0.6 cm; Malone et al., 2001) boundary layer in the matrix. Transfer between mobile and immobile subregions of the matrix is calculated as a diffusion-like process. RZWQM supplies default values for essential parameters for the active ingredient of most commercial pesticides. Management options include crop rotations schemes, tillage, irrigation, and applications of fertilizer, pesticide and manure. Additional features are listed in Table 1. Further descriptions of RZWQM components and recent applications can be found in Malone et al. (2004a), Wauchope et al. (2004), and Ma et al. (2007).

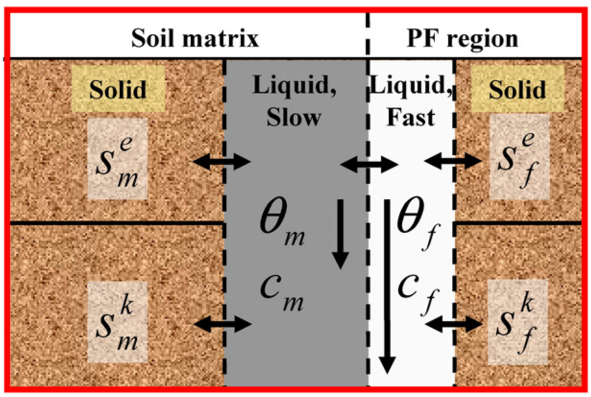

Fig. 3. Model concept of physical non-equilibrium (lateral solute transfer) and chemical non-equilibrium (kinetic sorption) in a dual-permeability medium (modified after Šimůnek and van Genuchten, 2008); in the plot, θ_m and θ_f are water contents of the matrix and macropore (fracture) regions, respectively; c are concentrations of the corresponding regions, s_e are sorbed concentrations in equilibrium with the liquid concentrations of the corresponding regions, and s_k are kinetically sorbed solute concentrations of the corresponding regions. Less general model concepts neglect some processes (e.g., matrix region is considered to be immobile, or only equilibrium sorption is considered, etc.).

2.2. MACRO

The MACRO model (Jarvis, 1994; Jarvis et al., 2003; Larsbo and Jarvis, 2003, 2005) also is an agricultural systems model with particular focus on macropore flow processes. The dual-permeability model (DPM) can describe sorption as an instantaneous equilibrium or a two-site equilibrium-kinetic process (kinetic sorption in the matrix only). The same Freundlich adsorption isotherm is assumed for both micro- and macropores, with the total sorption partitioned into two fractions for the two domains. The sorption characteristics can be adjusted at a number of dates during the simulation to mimic sorption aging. Exponential pesticide degradation can be calculated separately for the solid and liquid phases of both domains, while degradation parameters can be adjusted for temperature and moisture effects. Lateral solute transfer between the macropore domain and matrix is calculated as a first-order rate approximation to the advection-diffusion equation. Jarvis et al. (1997) developed the pesticide modelling tool MACRO_DB by linking databases of soils, pesticide properties, climate and crop data to MACRO, and by including sets of pedotransfer functions and other parameter determination rules. The purpose of MACRO_DB is to facilitate the predictive application of MACRO. For additional features see Table 1.

2.3. HYDRUS-1D/-2D/(2D/3D)

The HYDRUS-1D model package (Šimůnek et al., 1998, 2003, 2005; Šimůnek and van Genuchten, 2008) is a process-based model simulating water, heat, and solute movement in the vadose zone. In the latest version, the mobile-immobile water content model (MIM) and different DPM approaches (Gerke and van Genuchten, 1993) were included and extended to calculate preferential transport of a parent pesticide and its metabolites formed by first-order degradation. Actual decay rates can be calculated as functions of temperature and soil moisture, for dissolved and solid phases, in the PF region and the matrix (or the immobile region). Sorption can be described using linear, Freundlich, or Langmuir isotherms for equilibrium, one- or two-site kinetic sorption, assumed to be either similar or different in the different soil regions (Fig. 2). First-order terms for bi-directional exchange of water and solute are used (for additional features see also Table 1).

Multi-site sorption concepts that can consider kinetic, irreversible, and attachment-detachment approaches were also implemented (e.g., Wehrhan et al., 2007), as well as particle (e.g., Bradford et al., 2003) and colloid-facilitated solute transport (Šimůnek et al., 2006a,b) options, but so far only for the equilibrium Richards and CDE based models in HYDRUS-1D. The HYDRUS-2D model package (Šimůnek et al., 1999), and its latest update HYDRUS (2D/3D) (Šimůnek et al., 2006b), are the two- and two/three-dimensional equivalents of HYDRUS-1D, respectively. Additional features in HYDRUS-2D concern boundary conditions (e.g., tile drainage) and tools for calculating spatially distributed model parameters.

2.4. SIMULAT

The model SIMULAT (Diekkrüger, 1996) is a 1D DPM that considers sorption in the matrix using equilibrium or kinetic forms of Freundlich or Langmuir isotherms. The model can

Table 1
Characteristics of common 1D models for preferential transport of pesticides

	RZWQM	MACRO	HYDRUS-1D[a]	CRACK-NP	SIMULAT	PLM
Documentation	Ahuja et al. (2000a,b), Malone et al. (2004a), Wauchope et al. (2004), Ma et al. (2007)	Larsbo and Jarvis (2003, 2005)	Šimůnek et al. (2005), Šimůnek and van Genuchten (2008)	Armstrong et al. (2000b)	Diekkrüger (1996)	Hall (1994), Nicholls and Hall (1995)
Model concept (s)	DPM, DP-MIM	SPM, DPM	SPM, MIM, DPM, DP-MIM	MIM	DPM	DP-MIM
Solute transport						
a) Matrix	Convection, partial mixing	Convection–dispersion	Convection–dispersion	Immobile	Convection–dispersion	Immobile
b) PF domain	Convection, mixing (expon. depth decrease)	Convection	Convection–dispersion	Convection	Convection	Convection
Solute transfer						
a) PFdomain-matrix	Instant mixing with a boundary matrix layer	First-order advection–diffusion	First-order advection–diffusion	Advection (Philip)–diffusion (Fick)	Advection (Darcy)	Advection
b) Matrix-Pfdomain	Instant mixing with a boundary matrix layer	Advection (routing), first-order diffusion	First-order advection–diffusion	Diffusion-like[c], Peds-peds/peds-PFdomain	Advection(?)[c]	–
c) DP-MIM: mo-im	First-order diffusion	–	First-order diffusion	–	–	Diffusion-like[c]
Sorption						
a) Matrix	Linear, Freundlich, three-site (equilibrium, kinetic, bound or aged residues, pH-dependence)	Linear, Freundlich, two-site (equilibrium, kinetic), aging approximation	Linear, Freundlich, Langmuir, two-site (equilibrium, kinetic)[b]	Linear, Freundlich, (equilibrium)	Linear, Freundlich, Langmuir, (equilibrium, three sites)	Linear, (equilibrium), aging approximation in top 5 cm
b) PFdomain	No	Linear, Freundlich	Linear, Freundlich, Langmuir, two-site (equil.-kin.)	No	No	No/Yes (only in slow mobile water)
Degradation						
a) Matrix	First-order, function of T, θ (aerobic or anaerobic)	First-order, function of T, θ	First-order, function of T, θ; Degradation on solid	First-order, function of T, θ	First-order or Michaelis Menten or (co)metabolic, function of T, θ	First-order, function of T, θ
b) PFdomain	No	first-order, function of T, θ	First-order, function of T, θ; Degradation on solid	No	No	No
Heat flux	Yes	Yes	Yes	No	Yes	No
Root growth	Yes	Yes	Yes	Yes	Yes	Yes
Root uptake	Water, Solute	Water, Solute	Water, Solute	Water	No	No
Volatilization	Yes	(Yes)—lumped dissipation rate	Yes	No	No	No
Surface runoff	Yes	(Yes)	(Yes)	(Yes)	No	No
Solute in runoff	Yes	No	No	No	No	No
Management options	Crop rotations, tillage, fertilizer, manure, pestic. application mode	Tillage	No	No	No	No
Tile drainage	Yes	Yes	Yes	(Yes)	Yes	(Yes)
Inverse method	No	SUFI	Levenberg–Marquardt	No	No	No
GUI	Yes	Yes	Yes	No	No	No
Selected further features	Pesticide degradation on crop foliage and residue, crop growth and yield, organic matter and nutrient cycle, ion dissociation, chemical transfer to surface runoff, erosion	Swell-shrink dynamics, compaction, surface sealing, pesticide intersection canopy dissipation and washoff, uncertainty estimation, metabolites	Particle transport, CO_2 transport, chemistry of carbonate system, major ion chemistry, metabolites	Swelling-shrinking, canopy interception		Time step is 1 day, space increment is 5 cm, no groundwater table

(ET—evapotranspiration, T—temperature, mo—mobile region, im—immobile region, PF—preferential flow, K_D—Sorption distribution coefficient, θ—soil moisture content, (Yes) means: is considered, but in a simplified way, SPM—single porosity model, MIM—mobile-immobile water model, DMP—dual-permeability model, DP-MIM—dual-permeability model with immobile water), GUI—Graphical User Interface.

[a]Similar features are included in HYDRUS-2D and HYDRUS (2D/3D).

[b]Multi-site sorption concepts such as kinetic, irreversible, and attachment-detachment based approaches are included in a special HYDRUS-1D versions (e.g., Wehrhan et al., 2007).

[c]In publications, the equations used for process description were not indicated.

consider up to three different sorption sites. Pesticide degradation can be of exponential, Michaelis–Menten, metabolic or co-metabolic type, and can depend on soil moisture and temperature. Water and solute exchange between macropores and matrix is represented as a first-order rate process. Plant growth, heat transport and tile drainage can also be simulated (Table 1).

2.5. CRACK-NP

CRACK-NP (Armstrong et al., 2000b) describes water flow and the transport of tracers, nitrate or pesticides in clay soils with shrinkage cracks. Sorption can be described as a linear or Freundlich equilibrium process, while the first-order degradation is calculated according to Walker and Barnes (1981) and depends on soil temperature (Arrhenius equation) and moisture. Crop height and root depth increase at a constant rate after crop emergence until they reach a maximum value (Armstrong et al., 2000b).

2.6. PLM

The Pesticide Leaching Model (PLM, version 3) developed by Hall (1994) and Nicholls and Hall (1995) is a relatively simple capacity model, which assumes that water moves downward in the soil profile in the 'tipping-bucket' fashion. PLM uses discretization layers of 5-cm thickness and a calculation time interval of one day. The soil is divided into fast mobile, slow mobile, and immobile regions. The mobile and immobile domains are divided by a pressure set at −5 kPa (field capacity). The percentage of the fast mobile phase (air capacity) is an empirical input parameter, and is constant for all horizons, irrespective of their different characteristics. In the top numerical layer, solute is at equilibrium between liquid and solid phases in all regions. In lower layers, lateral equilibration is governed by water and advective solute exchange between the regions. Linear equilibrium sorption is assumed. Sorption in the top layer increases gradually with time to simulate aging or diffusion effects. First-order degradation is calculated as a function of the soil depth, temperature and soil water content. One soil layer can be specified to contain drains and a specified percentage of the water reaching this layer can flow into the drains, while the remainder continues to seep downwards.

2.7. Other approaches

The DPM of Gerke and van Genuchten (1993) based on the Richards and convection–dispersion equations for both the matrix and fracture pore regions was extended by Ray et al. (1997, 2004) to simulate pesticide leaching. The resulting S1D DUAL model allows for biodegradation, and for linear equilibrium and kinetic pesticide sorption. Both of these processes can vary with soil depth and between flow domains. A sensitivity analysis was conducted to evaluate the effects of various parameters characterizing the preferential pesticide transport (Ray et al., 2004).

The ADAPT (Agricultural Drainage And Pesticide Transport) model of Chung et al. (1991a,b) is a capacity model that combines parts of the GLEAMS daily simulation model (Leonard et al., 1987) with the capability of accounting for subsurface drainage and subirrigation using DRAINMOD (Skaggs, 1980). Pesticides move upward in the flow region due to evaporation and downward due to macropore flow and infiltration. Linear pesticide sorption and degradation are calculated on a daily basis. Kalita et al. (1998) successfully tested ADAPT using field data collected in shallow groundwater under three water table management practices near Aimes, Iowa, USA. However, the effect of macropore flow was not discussed.

The WAVE model (Vanclooster et al., 1994) uses a simplified description of preferential transport. The Richards equation is used for calculating equilibrium water flow, and the MIM for describing solute transport. Heat transport is modelled based on Fourier's law. Root water uptake, linear equilibrium sorption, and first-order degradation adjusted for soil moisture and temperature are also considered.

LEACHM (Hutson and Wagenet, 1992) describes water flow and chromatographic solute transport using the Richards and convection–dispersion equations, respectively. LEACHM was used by Elliott et al. (1998) to consecutively simulate independent matrix and PF region transports. The results of the two simulations were then combined to yield an approximate DPM (without mass transfer between regions) simulation of preferential solute displacement (Elliott et al., 1998).

Discrete fracture models (DFM) were primarily designed for saturated flow and transport in the fractured rock. FRACTRAN (Sudicky and McLaren, 1992) is a 2D model that assumes DARCY's flow and convection–dispersion transport in the matrix, while the cubic law and CDE are used to model flow and transport in the fractures. Linear sorption and first-order degradation can also be considered. FRACTRAN was applied to simulate pesticide transport in clayey till (Jørgensen et al., 1998).

Several specific laboratory scale research models have been designed to analyse and better understand selected processes. For instance, to understand the nonideal solute transport, relative contributions of nonequilibrium processes related to physical heterogeneity versus those related to rate-limited sorption need to be determined (Johnson et al., 2003).

Combined PNE and CNE descriptions were also implemented, in addition to models discussed above (e.g., MACRO and HYDRUS-1D), into steady-state transport models developed by Selim and his collaborators (e.g., Selim and Ma, 1997; Selim et al., 1999, 2002; Zhou and Selim, 2001; Ma and Selim, 2005). The second-order two-site kinetic sorption model (SOTS) assumes that sorption rates depend on both solute concentrations in the solution and the availability of adsorption sites in the matrix. Different SOTS models (CNE) were coupled with the MIM (PNE) to form the SOTS-MIM models (Selim et al., 1999). Additionally, the multireaction model (MRM) considers Freundlich equilibrium sorption, kinetic sorption with different first-order rates for ad- and desorption, and irreversible sorption. The MRM was also coupled with the MIM to form the MRM-MIM model (Selim and Ma, 1997).

The Lattice Boltzmann Model (LBM) was extended to simulate transport of reactive solutes such as pesticides by Zhang and Ren (2003). The LBM simulates the local-scale transport process by numerical particle tracking in space and time according to physically based collision rules that preserve mass and momentum. Tracking directions can be upward, downward, and (internally) horizontal to allow for instantaneous ('inner' wall) and kinetic ('outer' wall) sorption reactions (Zhang and Ren, 2003).

3. Model application

3.1. Scale I (Soil column, lysimeter)

Repacked soil columns with artificial PF paths were utilized as well-defined systems to facilitate the analysis of the complex pesticide transport behavior. Steady-state flow conditions were often chosen to further simplify the problem (Section 3.1.1). On the other hand, intact (undisturbed) soil columns preserve the natural soil structure, and thus better represent the field soil conditions. Lysimeters, because their dimensions are larger than laboratory soil columns and are often constructed in field settings, best represent the local field conditions (Section 3.1.2). Therefore, lysimeters are used in European countries as a higher tier for assessing the groundwater contamination potential of pesticides (Boesten, 2007). Pesticide transport in undisturbed soil columns and lysimeters was studied under both steady-state and transient flow conditions.

Solute transport models were often evaluated using the analysis of collected breakthrough curves (BTC). A difficulty with this approach is that PNE and CNE may sometimes cause similar or even identical irregularities in the BTC shape (Nkedi-Kizza et al., 1984; Selim et al., 1999). Classical methods of distinguishing between PNE and CNE in BTC analysis involve applying a tracer together with the pesticide, measuring the sorption behavior in separate batch and kinetic tests, and evaluating degradation in incubation experiments. Physical transport processes at this scale are most often described using two-domain 1D approaches, which are combined with different submodels accounting for chemical processes, such as equilibrium or kinetic sorption and other pesticide related reactions. Degradation is described mostly as a first-order rate process (Beulke et al., 2000). An overview of model applications at scale I is given in Table 2.

3.1.1. Constructed soil columns

Transport experiments with artificial and repacked soil columns were conducted to identify model oversimplifications and potential misinterpretations of model results. For example, the BTCs of a tracer and hydrophobic organic compounds that leached through a cylindrical macropore filled with quartz sand embedded in the silty soil matrix were well matched using a MIM with assumed equilibrium sorption (Rahman et al., 2004). However, the fitted sorption coefficients (K_D) were up to 80% lower than those for batch experiments, which was explained

Table 2
Applications of models simulating preferential pesticide (or reactive solute) transport at scale I

Scale	Model type; name	Model dimension, model description (as applied)[a]	Reference (Scale)
AC	MIM; n.a.	1D, steady-state, advection in the mobile region, diffusive transfer, linear equilibrium sorption (2×)	Rahman et al. (2004)
AC	SOTS, MRM, SOTS-MIM, MRM-MIM, SPM	1D, steady-state, SOTS-MIM with two-site sorption kinetics (2×), or MRM-MIM with multiple sorption reaction rates	Selim and Ma (1997), Selim et al. (1999), Selim et al. (2002)[c], Ma and Selim (2005)
AC[b]	MIM; CXTFIT	1D, steady-state, MIM, transfer: first-order or radial diffusion, spherical or cylindrical geometry, linear equilibrium sorption (2×)	Young and Ball (1997, 2000)
AC	Lattice Boltzmann Model (LBM)	1D, microscopic numerical particle tracking in space and time, equilibrium and kinetic sorption	Zhang and Ren (2003)
UC[b]	DPM; S-1D-DUAL	1D, Richards (2×), CDE (2×), first-order transfer of water and solute, linear equilibrium and kinetic sorption (2×), first-order decay (2×)	Ray et al. (2004)
UC	MIM with two-site sorption; n.a.	1D, mobile–immobile water flow, MIM with sorption kinetics (2×), first-order decay (2×)	Gaston and Locke (2000)
UC	DPM; Root Zone Water Quality Model (RZWQM)	1D, Poiseulle, convection (macropore), Green-Ampt, convection (matrix), nonlinear and kinetic adsorption (matrix), decay (matrix), plant uptake (matrix)	Malone et al. (2001, 2003, 2004a,b,c)
UC	SPM, MIM, DPM, DP-MIM; HYDRUS-1D	1D, Richards (1–2×), CDE (2×) or MIM, first-order transfer of water and solute, nonlinear equilibrium and kinetic sorption (2×), degradation (2×)	Pot et al. (2005), Köhne et al. (2006a,b), Javaux et al. (2006)
UC, L	DPM; MACRO	1D, KW, convection (macropore), Richards, CDE (matrix), linear equilibrium sorption (2×), first-order decay (2×); inverse tools: SUFI, GLUE	Beulke et al. (2004) (UC); Roulier and Jarvis (2003a,b) (UC); Brown et al. (1999) (L); Dubus and Brown (2002) (L)
L	MIM (Solute); WAVE	1D, Richards (1×), MIM, diffusive transfer	Vereecken and Dust (1998) (L)
L	DFM; FRACTRAN and FRAC3Dvs version 4.0	2D (FRACTRAN) and 3D (FRAC3Dvs), steady-state, Darcy, CDE, first-order decay, linear sorption (matrix), cubic-law flow between parallel plates, advection (fracture), diffusive transfer	Jørgensen et al. (1998)
L	DPM; SIMULAT	1D, Richards, CDE (matrix), gravity film flow, convection (macropores), sorption (matrix): Freundlich, decay (matrix): first-order or metabolic	Stange et al. (1998), Aden and Diekkrüger (2000)
L	Model reviews and comparison: MIM, DPM; e.g. SWAT, MACRO, MACRO_DB, CRACK-NP, SIMULAT, PLM	various 1D nonequilibrium transport models, topics: model performance, inverse parameter estimation, uncertainty, user subjectivity, transferability of lab measured data (e.g., pesticide degradation rates) to the field	Francaviglia et al. (2000), Vanclooster et al. (2000a,b), Dubus et al. (2003a,b), Gottesbüren et al. (2000)

Artificial or Repacked Soil Column (AC), Undisturbed Column (UC), Lysimeter (L), CDE—convection–dispersion equation, SPM—single porosity model, MIM—mobile immobile model, DPM—dual permeability model, TPM—triple permeability model, KW—kinematic wave, PF—preferential flow, SOTS—second-order two-site model, MRM—multireaction model, (2×)—double; refers to the matrix and PF path regions.
[a]Model applications may differ from full model capabilities; only flow, transport, fate (plant–atmosphere interactions are not mentioned).
[b]Synthetic model parameters.
[c]Transient flow.

as a model artifact revealing rate-limited sorption (CNE) during PNE-PF (Rahman et al., 2004). Moreover, under unfavorable conditions the solute retardation factor and the first-order transfer coefficient in MIM may be interdependent (Young and Ball, 1997). Temporal moments calculated for reactive solute BTCs from a macropore column further suggested data truncation as yet another reason for column-determined retardation factors being lower than batch-estimated values (Young and Ball, 2000).

The predictive capabilities of various models (MIM, SOTS-MIM, MRM, MRM-MIM) were tested to describe atrazine BTCs for different pore water velocities, aggregate sizes, flow interruptions, and lengths of repacked clay soil columns. On average, SOTS-MIM with four parameters and a time-dependent mass transfer coefficient best described atrazine transport in these clay soil columns (Selim and Ma, 1997). Selim et al. (1999) further compared the performance of SOTS and SOTS-MIM for simulating the transport of metolachlor in clay soil columns. To trigger nonequilibrium conditions, the column experiments were conducted for different aggregate sizes and with flow interruptions. Sorption model parameters were independently derived from kinetic ad- and desorption batch experiments. Model predictions of metolachlor BTCs improved after ad-/desorption hysteresis was included in the model. Again, the best predictions were obtained using SOTS-MIM (Selim et al., 1999). Additionally, these and modified model approaches were applied to experimental data obtained on columns packed with other soils, in layered soil systems (Zhou and Selim, 2001), to atrazine transport in soil–mulch systems (Ma and Selim, 2005), and to alachlor transport in variably-saturated soil columns subject to transient flow (Selim et al., 2002).

Zhang and Ren (2003) compared simulation results obtained using their 1D Lattice Boltzmann Model (LBM) with measured Br^- and atrazine BTCs, and against the two-site sorption model. There was close agreement between the collected data and both models. However, tremendous effort would be required to expand the LBM to simulate pesticide transport in real agricultural field settings (Zhang and Ren, 2003).

3.1.2. Undisturbed soil columns and lysimeters

A large number of studies involving modelling of pesticide transport in intact soil cores or lysimeters utilized RZWQM, HYDRUS-1D, or MACRO. Therefore applications of these models are described first. Applications of various other models are summarized thereafter.

3.1.2.1. Root Zone Water Quality Model (RZWQM). Although the RZWQM (Ahuja et al., 2000a,b) was intended mostly for field scale applications, some of its individual model components were evaluated at the column scale. For example, Malone et al. (2001) assessed the performance of the macropore component of RZWQM in simulating atrazine and alachlor transport in no-till soil blocks for dry, intermediate, and wet initial moisture states. Even though simulated chemical concentrations in percolate were within a factor of 2 of observed values, their observed and simulated patterns were quite different. It was suggested that the macropore component of RZWQM could be improved by considering sorption kinetics in macropores and a dynamic effective macroporosity that would increase with greater rainfall (Malone et al., 2001).

Using RZWQM, Malone et al. (2003) studied the effects of tillage (moldboard plowed and no-till) on the macroporosity of undisturbed silt loam soil blocks, and on alachlor and atrazine transport in percolate. Although the number of macropores was similar in both soil blocks, the initial percolate breakthrough was faster with higher herbicide concentrations in the no-till soil than in the moldboard plowed soil. Modelling results suggested that lower values of the saturated hydraulic conductivity of the soil matrix, which reduced lateral transfer between macropores and the matrix, caused rapid water percolation and breakthrough in the no-till soil. However, this statement cannot be generalized. Evidence from many other studies points to the importance of large vertically continuous macropores formed by anecic earthworms under no-till as the reason for this (see discussion in Jarvis, 2007). For the same soil, Malone et al. (2004b) used RZWQM to analyze the effects of variable rainfall intensity on pesticide transport through macropores. The variable-intensity storm quadrupled simulated alachlor losses and doubled atrazine losses when compared to the constant-intensity storm of the same total depth (Malone et al., 2004b). The significant effect of within-storm variability on simulated macropore flow was confirmed by Struthers et al. (2007), based on detailed DPM scenario simulations.

Malone et al. (2004c) simulated the effect of the RZWQM parameter 'nmacro', which defines the number of percolate-producing macropores, on breakthrough time and concentrations for the first storm after application. They used observations of alachlor and atrazine leaching in 39 intact soil blocks sampled from five no-till and moldboard plowed fields. Increasing nmacro decreased the simulated leached herbicide concentrations and increased breakthrough time (Malone et al., 2004c). This somewhat counterintuitive result shows that proper application of a model requires detailed understanding of the underlying concepts. The explanation here is that when nmacro is increased, the RZWQM-simulated macropore flow is distributed among a greater number of macropores, which in turn increases the total macropore wall area available for equilibration with the matrix.

3.1.2.2. MACRO. Brown et al. (1999) applied MACRO 4.0 to simulate isoproturon leaching as observed in a lysimeter experiment. A radioscanning technique and dye tracer were used to assess the movement of radiolabeled isoproturon in a macroporous heavy clay soil with different tilth systems. At an 8-cm depth, only 0.5% of the soil area showed increased activity. Thus, preferential movement was already initiated within the top 10 cm. Rhodamine-B red dye then spread laterally across the topsoil–subsoil layer boundary, and appeared in cracks and fissures in the subsoil. The dye was found only in a small part of the total crack surface area, and thus was adsorbed only along that part of the macroporosity. The applied MACRO version 4.0 accounts for equilibrium sorption in matrix and macropores. The simulation was successful only after calibrating the fraction of sorption sites in the macropores to a value of 0.01 (which may reflect the sorption in only part of the macroporosity or kinetic effects), and varying the half-width (aggregate size) parameter for fine and standard tilth (Brown et al., 1999).

Strömqvist and Jarvis (2005) applied MACRO to analyze leaching of the fungicide iprodione in a golf green. MACRO matched the measured drainflow and iprodione concentrations in the soil and drainflow reasonably well. Underestimated peak concentrations were attributed to finger flow caused by water repellency (Strömqvist and Jarvis, 2005).

3.1.2.3. HYDRUS-1D. Pot et al. (2005) used HYDRUS-1D to analyze the impact of different constant rainfall rates on Br^-, isoproturon, and metribuzin leaching in undisturbed soil cores collected from the grassed filter strip. Various approaches, including DPM, MIM, DP-MIM, and DPM with kinetic sorption, were compared to simulate the observed BTCs. Observations showed a strong impact of rainfall intensity on Br^- and herbicide leaching. At the highest rainfall intensity, macropore flow caused rapid chemical breakthrough. The DP-MIM simulation results best approximated the observed Br^- breakthrough, suggesting that three porosity domains contributed to transport at the high rainfall intensity. At lower rainfall rates, the less rapid preferential transport could be described well using two-region (MIM or DPM) approaches. Herbicide transport was affected by kinetic sorption at all flow velocities. Significantly higher estimated values for degradation rate parameters, as compared to batch data, were correlated with the extent of non-equilibrium sorption (Pot et al., 2005).

Similarly, Köhne et al. (2006a) applied HYDRUS-1D, further modified for transient flow conditions, to simulate transport of isoproturon, terbuthylazine and Br^- observed in an aggregated loamy soil column subject to several irrigation-redistribution cycles. First, forward simulations of herbicide transport were conducted using model parameters derived from the Br^- transport experiment, literature data for herbicide degradation, and equilibrium batch or kinetic sorption experiments. The early isoproturon breakthrough in the soil could be qualitatively predicted when using the DPM with two-site kinetic sorption. The subsequent inverse simulation suggested fewer equilibrium sites and slower sorption in the PF paths than was measured for the bulk soil in batch tests. This suggests that batch tests with disturbed soil cannot be used to derive accurate sorption parameters for intact structured soils. Moreover, degradation and sorption rate coefficients were highly correlated, had similar effects on the BTC, and thus could not be estimated simultaneously when using only the leaching BTC. As a result, the small fitted isoproturon half-lives of only a few days may have been a model artifact reflecting irreversible sorption (Köhne et al., 2006a). Pot et al. (2005) report several studies that estimated higher degradation rates for soil columns than obtained in incubation tests, which could be uncertain unless resident final resident concentrations were additionally measured. Malone et al. (2004d, see below) analyzed the effects of having equilibrium or kinetic sorption models on the simulated degradation in RZWQM. The uncertainty in corresponding parameters in MACRO was analyzed in detail providing additional insights (see Section 3.2.3), which will be discussed together with the above findings.

3.1.2.4. Other models. A sensitivity analysis was conducted using S-1D-DUAL to evaluate leaching of strongly sorbed trifluralin and weakly sorbed atrazine through a hypothetical 1-m deep soil profile. The results suggested that displacement of pesticides is strongly affected by the sorption rate in the PF paths and the decrease of sorption with depth (Ray et al., 2004).

Gaston and Locke (2000) examined the sorption, degradation, and mobility of the post-emergence herbicide acifluorfen measured in silty clay loam soil columns for steady-state unsaturated flow. The early Br^- BTC was matched well using the MIM, which suggested PNE. Using the fitted Br^- transport parameters and measured sorption isotherms and kinetics, the acifluorfen effluent BTC and the residual ^{14}C in the column were better predicted with the MIM and assuming two-site kinetics than with the Freundlich equilibrium sorption. Neither model, however, captured the long tailing in the BTC. Compared to the batch and incubation studies, it became apparent that more acifluorfen was residually bound and its degradation was faster in the soil columns (Gaston and Locke, 2000).

Vereecken and Dust (1998) applied WAVE (Vanclooster et al., 1994) with a Monte Carlo method to assess the effect of soil heterogeneity on leaching of the herbicide [14C-] methabenzthiazuron (MBT) as observed in five replicate lysimeters and in the field. Considering the spatial variability of soil hydraulic properties and of degradation parameters obtained in laboratory experiments resulted in extremely large variability of predicted MBT residues in the soil (Vereecken and Dust, 1998).

SIMULAT (Diekkrüger, 1996) was evaluated in two different lysimeter studies. Stange et al. (1998) carried out lysimeter experiments to study pesticide transport through five undisturbed macroporous silt loam monoliths (1 m height, 0.30 m diam.). The herbicides chlorotoluron and MBT were applied, together with Br^-, to these soil monoliths. While SIMULAT's soil hydraulic parameters were derived from measurements and sorption parameters taken from the literature, macropore parameters were fitted manually. SIMULAT reproduced soil water suctions and depth distributions of Br^- and both herbicides well. It was concluded that the macropore continuity between the plough horizon and the subsoil controls bypass flow (Stange et al., 1998).

Aden and Diekkrüger (2000) evaluated SIMULAT using three field datasets and one lysimeter dataset for a macroporous loam soil at Tor Mancina, Italy. For the lysimeter dataset, soil hydraulic parameters were manually calibrated and the longitudinal dispersivity was set at 10 cm. Sorption and degradation parameters were taken from the literature and lab experiments. Neither tracer and metolachlor concentrations in the leachate, nor their concentrations in the soil profile, were matched well. It was argued that the results do not necessarily invalidate SIMULAT for this soil, but that it is often not possible to distinguish between the model quality and user experience (Aden and Diekkrüger, 2000).

Jørgensen et al. (1998) applied the 2D discrete fracture model (DFM) FRACTRAN (Sudicky and McLaren, 1992) to study the migration of the herbicides mecoprop and simazine, together with Cl^- and fluorescent dye, in three undisturbed, water saturated, fractured clayey till columns (0.5 m high, 0.5 m diam.). Transport experiments were conducted at different flow velocities. Dye was observed in nearly all the visible, weathered fractures, as well as in the root channels. The saturated hydraulic conductivity of the columns decreased with increasing depth and fracture spacing. Using measured fracture spacing and calculated hydraulic aperture values (27–84 μm), assuming no degradation, and fitting retardation factors (assumed to be similar in the fractures and matrix), FRACTRAN predicted the observed flow and pesticide transport in all columns. The retardation of mecoprop and simazine decreased with increasing flow rate. At high flow rates, pesticides arrived simultaneously with Cl^-, suggesting PF and rate-limited sorption (Jørgensen et al., 1998).

Furthermore, particle-facilitated displacement of pesticides in the PF pathways may be quantitatively important in some field soils, such as Colluvisols with deep penetrating earthworm burrows (Zehe and Flühler, 2001), but it was hardly considered in modelling studies (e.g., Villholth et al., 2000).

3.1.3. Sensitivity, calibration, uncertainty at scale I

As was seen above (Pot et al., 2005; Köhne et al., 2006a), inverse identification of pesticide parameters, which moreover can differ between flow regions, can become a very difficult problem in modelling preferential pesticide transport. Studying the parameter sensitivity and uncertainty can suggest reasons behind the identification problems, and indicate the type of experimental information additionally needed for parameter identification. For this purpose, MACRO was used (Sohrabi et al., 2002; Dubus and Brown, 2002; Roulier and Jarvis, 2003a,b).

Roulier and Jarvis (2003a) assessed the performance of the optimization technique SUFI (Abbaspour et al., 1997) for estimating values and the associated uncertainty of 9 key MACRO parameters controlling pesticide transport. Undisturbed soil columns (20 cm height, 20 cm diam.) were sampled from the hilltop, slope, and hollow positions of a field in a loamy moraine catchment in South Sweden. Leaching experiments with Cl^- and the mobile herbicide MCPA were performed under transient flow conditions during a 4-month period. Rapid MCPA leaching through the fine-textured hilltop soil showed evidence of PF, while MCPA leaching was minimal in the organic-rich hollow soil. The MACRO-SUFI results closely followed the observed patterns of percolation and breakthrough of Cl^- and MCPA. Interestingly, MACRO parameter estimates varied significantly between different landscape positions and were clearly related to the soil texture and organic matter content. Such relations showed potential for use in pedotransfer functions (Jarvis et al., 2007). Sorption and degradation parameters could be identified. The short MCPA degradation half-lives of only 1–2 days obtained in the latter study were subsequently confirmed in incubation studies (Lindahl et al., 2005). However, significant uncertainties remained for some key parameters thought to be important for solute transfer and preferential leaching, including the saturated matrix conductivity and the mass transfer coefficient. To reduce these uncertainties, three changes were suggested. These were (i) to increase the number of strata during the last few optimization iterations to maintain the sensitivity of the objective function to the optimized parameters, (ii) to use posterior uncertainty domains to define initial values in a subsequent gradient-type optimization procedure, and (iii) to improve experimental designs (Roulier and Jarvis, 2003a).

In a follow-up study using MACRO-SUFI, Roulier and Jarvis (2003b) used numerically generated data representing similar experiments to quantify, among others, the effect of experimental errors on inverse model simulations. Although experimental errors increased the uncertainty of estimated coefficients, optimized parameters were still properly identified. However, MACRO results were reliable only when strong macropore flow was present and when both resident and flux concentrations were utilized in the inverse procedure. Once again, the mass transfer coefficient was insensitive to model predictions and highly uncertain. Adsorption and degradation parameters could not be estimated accurately due to their large mutual correlation (Roulier and Jarvis, 2003b). Similar problems were also experienced (e.g., Pot et al., 2005; Köhne et al., 2006a) when using the DPM (Gerke and van Genuchten, 1993) in HYDRUS-1D.

Moreover, the MACRO-SUFI performance depended on whether water and solute parameters were estimated simultaneously or sequentially. The best results were achieved for a simultaneous parameter estimation procedure when the goal function included water percolation, the leaching rate, and resident concentrations for both tracer and pesticide (Roulier and Jarvis, 2003b). Using HYDRUS-1D, similar results were found for tracer transport (Köhne et al., 2006b).

It can be considered as a modelling progress that inverse estimation pitfalls and uncertainty issues could be identified, since this can help in the development of improved experimental designs. Inverse DPM applications require both resident and flux pesticide concentrations, as well as water flow and tracer data, to describe degradation and sorption in structured soils. But even then, inverse identification of these processes for individual flow regions is often subject to large uncertainty. In the case of tracer transport, computer tomography and dye tracing could provide the additionally required information (e.g., Vanderborght et al., 2002—see companion paper (this issue)), although at a substantial experimental effort. It could be tested if independent sorption and degradation measurements in macropores, or with material from macropore walls, could provide independent estimates of the corresponding DPM parameters.

Experimental studies of the sorption properties of crack walls, earthworm burrows, and root channels were completed by e.g. Bundt et al. (2001a,b,c), Turner and Steele (1988), Stehouwer et al. (1994), and Mallawatantri et al. (1996). Bundt et al. (2001a,b,c) found for different soils that the cation exchange capacity, the base saturation, and the SOM content were all significantly larger in the dye stained PF paths than in the soil matrix, while sorption was enhanced for Cu but not for Sr (Bundt et al., 2001a,b,c). Dye stained PF paths had higher microbial biomass carbon contents, lower organic carbon, and lower affinity for dye (erioglaucine) sorption than the unstained soil (Gaston and Locke, 2002). Total and water soluble organic carbon contents, alkaline phosphatase activity, and atrazine ad- and desorption constants were found to be elevated in earthworm burrow linings compared with bulk soil, and pH and clay content of lining material were less variable than of the bulk soil (Stehouwer et al., 1993). The microbial degradation of isoproturon in the subsoil earthworm burrows was characterized by a half-life of 15 days and was almost as fast as in the topsoil. In the surrounding soil matrix, no degradation at all was observed within 30 days (Bolduan and Zehe, 2006). These results confirmed earlier findings of faster degradation of pesticides in macropore walls compared with the respective bulk soil or matrix materials (Stehouwer et al., 1994 (earthworm burrows); Pivetz and Steenhuis, 1995 (artificial macropores); Mallawatantri et al., 1996 (Bt macropore linings); Vinther et al., 2001 (red-ox structures)). Results about sorption in PF paths are less conclusive (see also discussion in Jarvis, 2007). When organic carbon content was higher, sorption was elevated. Macropores constitute a small volume fraction of structured soils.

However, when pesticide leaching is entirely constrained to macropores, then their local sorption and degradation properties control the leached fractions, together with lateral transfer and sorption in the matrix. As a complication, higher sorption and degradation capacities of macropore linings may not be fully exploited during PF conditions, due to limited contact time (rate limitation) or area (e.g., rivulet flow). The above experimental and modelling studies so far show that PF paths have distinct characteristics for retaining adsorbed and degradable pesticides, which cannot be characterized by the standard batch and incubation tests conducted with the bulk soil material.

Some of the studies below show that parameter sensitivity depends on context, such as length and time scales, boundary conditions, and soil type, which together control the transport pattern.

Stenemo and Jarvis (2007) conducted a Monte Carlo analysis of the uncertainty in pedotransfer functions used in MACRO simulations of pesticide leaching into groundwater. The saturated matrix conductivity and the mass transfer coefficient were the most sensitive parameters, together with the van Genuchten's (1980) parameters n and α. This divergence from the findings of Roulier and Jarvis (2003a,b) shows that the mass transfer coefficient is more sensitive for long-term simulations and deeper soil profiles, than it is for short term experiments carried out on short columns. Pedotransfer functions need to be improved to reduce uncertainties in model predictions (Stenemo and Jarvis, 2007). For example, for describing BTCs using MACRO, over half of the observed variation in the mass transfer coefficient could be explained by two basic soil properties related to soil texture and organic matter content (Jarvis et al., 2007).

Dubus and Brown (2002) studied the sensitivity and uncertainty of MACRO simulation results at the lysimeter scale as related to the variation of 43 (i.e., almost all) MACRO parameters in an exhaustive sampling. Two different approaches were compared for the sensitivity analysis: first, varying one parameter at a time (a "one-at-a-time" procedure), and second, a simultaneous variation of multiple parameters using the Monte Carlo analysis. Four base-case scenarios were generated by simulating the leaching of two hypothetical pesticides in a sandy loam and a structured clay loam soil during a four-year period. The accumulated water percolation and the accumulated pesticide mass leached to a 1-m depth were the model outputs used for the assessment of model sensitivity. Model sensitivities depended on the soil–pesticide combination. For the sandy loam, the Freundlich distribution coefficient, Freundlich exponent and degradation rate constant were most sensitive, and sorption and degradation were the main processes limiting pesticide leaching. For the clay loam, soil structure related parameters were even more sensitive, and controlled pesticide leaching. Due to PF, simulated pesticide losses were higher in the clay loam than in the sandy loam. The latter finding was corroborated by similar experimental observations in lysimeter studies conducted with these two soils (Beulke et al., 2001b). Four conclusions can be drawn from this study: (i) the choice of sensitivity investigation method may affect sensitivity results (the Monte Carlo analysis and the one-at-a-time procedure produced similar results for only two out of the four scenarios), (ii) the ranking of model parameter sensitivities is not universal, but depends to some extent on the soil and the substance, (iii) PF may cause higher pesticide losses from fine textured than coarser textured soils, and (iv) different processes control pesticide leaching in different soils. For the subsequent site-specific sensitivity analysis, the selection of the 10 to 15 most sensitive parameters from the results of this study was recommended (Dubus and Brown, 2002).

Uncertainty analyses can additionally indicate the effect of spatial variability on pesticide breakthrough. For example, consideration of uncertainty in MACRO input parameters resulted in a 20% higher simulated mean flow rate, along with two-to-three times larger atrazine leaching rates and concentrations, than when using mean input parameters (Sohrabi et al., 2002). While the uncertainty in predicted flow rates was relatively small, the uncertainty associated with the atrazine concentrations was an order of magnitude larger than that of the corresponding input parameters. Macropore flow related parameters contributed the most to the variability of atrazine transport results (Sohrabi et al., 2002).

Beulke et al. (2004) evaluated a probabilistic application of MACRO 4.1 to simulate leaching of isoproturon as observed during one winter in large columns (50 cm length, 25 cm diam.) containing sandy loam and moderately structured clay loam. Soil properties, and isoproturon sorption and degradation, were independently determined from soil samples. The uncertainty in model output distributions was compared with the experimental variability in seven replicates. For the sandy loam soil, varying only pesticide degradation and sorption properties allowed for matching of the observed variation of cumulative isoproturon leaching. By contrast, for the clay loam, the variability of selected soil hydraulic properties had to be considered additionally (Beulke et al., 2004). The latter result corroborated the findings of Dubus and Brown (2002) as described above.

Dubus et al. (2002b,a) discussed sources of uncertainty in pesticide fate modelling, such as (i) *uncertainty in the data* due to measurement errors or the spatial and temporal variability of environmental variables, (ii) *uncertainty in the derivation of model parameters*, such as the use of a wrong model (e.g., the application of first-order decay kinetics to data which do not follow this pattern), procedures to derive input parameters using limited information (e.g., pedotransfer functions), selection of a representative variable (e.g., arithmetic or geometric mean), inverse parameter estimation procedures and parameter non-uniqueness, and (iii) *uncertainties related to a model user*, including modeller's subjectivity in the choice of the pesticide fate model, the use of model concepts (e.g., K_{OC} is only established for non-ionic compounds, but often used for all molecules), or the parameterization of the model. Even techniques accounting for uncertainties are themselves subject to uncertainty. For instance, the overall results from Monte Carlo based probabilistic assessments may be influenced by the selection of input parameters, the probabilistic functions attributed to input parameters, correlations between parameters, and the sampling scheme used. It was suggested that those significant sources of uncertainty that are not currently considered, such as the model error and modeller's subjectivity, be integrated into probabilistic modelling exercises (Dubus et al., 2002b, 2003a). However, even if these suggestions could be realized, they seem likely to result in huge prediction uncertainty of little practical value.

Dubus et al. (2002a) provided a review on calibration of pesticide leaching models. The paper discusses data requirements, data quality assessment, the selection of a model and parameters for calibration, inverse techniques, how to compare simulated and measured data (e.g., visual and statistical assessments), calibration procedures, the assessment of calibrated parameter values, model validation, and uncertainty assessment (e.g., response surface analysis). Guidelines for calibration within the scope of pesticide registration were also proposed (Table 2 in Dubus et al., 2002a).

3.1.4. Model comparisons at column and lysimeter scales

Because of their increasing use in pesticide registration procedures worldwide, it is important to compare existing pesticide leaching models and to assess their ability to simulate pesticide transport, especially when subject to preferential flow processes (Scorza Junior and Boesten, 2005). Several studies compared different pesticide leaching models at scale I (e.g., Francaviglia et al., 2000; Gottesbüren et al., 2000; Vanclooster et al., 2000b).

Francaviglia et al. (2000) evaluated the five pesticide leaching models GLEAMS (Leonard et al., 1987), PELMO (Klein, 1995), SIMULAT (Diekkrüger, 1996), the Pesticide Root Zone Model PRZM-2 (Mullins et al., 1993), and VARLEACH (Walker and Hollis, 1994) against data collected on four lysimeters installed in a calcareous clayey loam soil in Rome, Italy. The soil water drainage and leaching of Br^- and metolachlor were monitored over a three-year period. None of the models compared could adequately describe monitored water, tracer and pesticide dynamics. Only SIMULAT, the single model that considered PF, reproduced the trace amounts of metolachlor observed during the first 2 years in the lysimeter leachates. However, the blind validation test for the third year failed even for SIMULAT, which predicted metolachlor leaching when none was observed (Francaviglia et al., 2000).

Herbst et al. (2005a) compared four other models, MARTHE (Thiéry et al., 2004, Thiéry, 1995), TRACE (Vereecken et al., 1994) coupled with 3dLEWASTE (Yeh et al., 1992), ANSWERS (Bouraoui et al., 1997), and MACRO 5.0 (Jarvis et al., 2003, Larsbo and Jarvis, 2003, 2005), by simulating vertical drainage and methabenzthiazuron (MBT) transport in a cropped free-draining lysimeter over the course of 627 days. After calibration, the models based on the Richards equation (MARTHE, TRACE, MACRO) predicted water flow better than the capacity model ANSWERS. Only the PF model MACRO could be calibrated to describe the MBT concentrations in the outflow. However, the difficulty in estimating parameters characterizing macropore transport remains an obstacle to common model applications (Herbst et al., 2005a).

Dubus et al. (2003b) conducted sensitivity analyses for three chromatographic models (PELMO, PRZM, PESTLA) and one PF model (MACRO) by simulating the leaching of two hypothetical pesticides in 1-m deep sandy loam and clay loam soils, respectively. The results depended greatly on the model type. In the chromatographic models, water flow predictions were controlled by atmospheric boundary conditions and the simulated pesticide loss was sensitive to sorption and degradation parameters. In MACRO, soil hydrological and PF related properties controlled pesticide leaching in the clay loam soil (Dubus et al., 2003b).

3.2. Scale II (plot, field)

3.2.1. Model concepts

While plots are usually considered homogeneous in model applications (apart from layering), cultivated soils at the field scale are often highly heterogeneous in terms of their physical and chemical properties. This heterogeneity results in spatially variable transport velocities and conditions for pesticide degradation and sorption. A common modelling concept describes the average field behavior deterministically without considering the internal spatial heterogeneity (e.g., 'integrated leaching response of a tile drained field'). This deterministic approach uses input data derived from laboratory measurements of pesticide and soil properties, in combination with weather, soil and crop information collected in the experimental field. However, since for nonlinear processes effective model parameters do not correspond with simple averages of measurements in the heterogeneous field (e.g., Vereecken et al., 2007; Vanderborght et al., 2006; Sohrabi et al., 2002; Lindahl et al., 2005), this approach theoretically requires model calibration. By contrast, a probabilistic approach termed here the 'nonlocalized stochastic' approach (e.g. Monte Carlo), does not use a single parameter set as an input for the deterministic model, but uses multiple parameter sets representing different realizations of random variables with corresponding probability distributions. This allows for uncertainty estimation in the ensemble of model simulation results, or for indirect characterization of spatial variability. On the other hand, stochastic distributed approaches describe the spatial variability in 2D or 3D transport models using geostatistical or spatial correlation functions. Table 3 provides an overview of model applications at scale II.

3.2.2. Deterministic model applications

3.2.2.1. Deterministic applications of the RZWQM. The RZWQM (Ahuja et al., 2000a,b) is frequently applied for field scale modelling of pesticide leaching. Malone et al. (2004a) reviewed many RZWQM applications for pesticide transport modelling. The review revealed the importance of (i) an accurate parameterization of low permeability soil horizons; (ii) considering pesticide sorption kinetics, and (iii) calibrating the pesticide half-life. If key input parameters were calibrated, RZWQM was found to match field observations of evapotranspiration, water percolation and runoff, soil water content, plant growth and pesticide fate (Malone et al., 2004a).

Ghidey et al. (1999) evaluated the performance of RZWQM 3.2 in predicting atrazine and alachlor loss to surface runoff in claypan soils with corn and soybean under conventional and no-till systems at a Management System Evaluation Area (MSEA) in Missouri, USA. Data from a 35-ha field, two 0.35-ha field plots and 40 smaller runoff plots (3 m by 27 m) were included in the study. Using the macropore option of RZWQM strongly improved the prediction of pesticide losses to seepage from lysimeters in the field plots. The measured soil water contents at several depths and annual runoff were adequately simulated, but runoff events in the drying soil with cracks were overestimated. For events where surface runoff was described well, atrazine and alachlor concentrations in surface runoff could be also simulated. It was suggested that RZWQM should

Table 3
Applications of models simulating preferential pesticide (or reactive solute) transport at scale II

Scale	Model type; name	Model dimension, Model description (as applied)	Authors (Scale)
S	DP-MIM; Pesticide Leaching Model vs.3 (PLM)	1D capacitance model, 5-cm layers, daily water balance, linear sorption (daily increasing in top 5 cm), first-order degradation = f(T,θ),	Nicholls et al. (2000) (S)
L, P	DPM; Agricultural Drainage And Pesticide Transport (ADAPT)[d]	1D, capacity-type macropore flow, convection, first-order decay, linear sorption, drainage	Kalita et al. (1998)
P[a,b]	MIM, DPM; n.a.	1D, steady-state, MIM-CDE or 2×CDE with spatial random variables K_s, K_D, degradation rate, diffusion transfer rate	Huang and Hu (2001), Hu and Huang (2002)
P	DFM; FRACTRAN and FRAC3Dvs version 4.0	2D (FRACTRAN) and 3D (FRAC3Dvs), steady-state flow: Darcy, CDE (matrix), cubic-law flow between parallel plates, advection (PF region), diffusive transfer, linear sorption (2×), first-order decay	Jørgensen et al. (2002, 2004)
P	SPM, DPM; HYDRUS-1D	1D, Richards (1–2×), CDE (1–2×), first-order transfer of water and solute, Freundlich sorption, degradation (2× in liquid and solid phase), root water uptake	Kodešová et al. (2005)
P	MIM, DPM, SPM; HYDRUS-2D	2D, Richards (1–2×), CDE (1–2×), first-order transfer of water and solute, linear sorption (1–2×), first-order degradation (1–2×, liquid and solid phase), root water uptake, crop effects, drainage	Gärdenäs et al. (2006)
P[a,b]	DPM with database; MACRO_DB	1D, MACRO with database for soils, pesticides, climates and crops; parameter determination routines	Jarvis et al. (1997)
F (S,P)	DPM; MACRO	1D, KW and convection (macropore), Richards and CDE (matrix), linear or Freundlich sorption (2×), first-order decay; Inverse tools: SUFI, GLUE	Jarvis et al. (2000) (S); Villholth et al. (2000) (P); Larsson and Jarvis (1999, 2000) (P)[a]; Brown et al. (2004), Larsbo and Jarvis (2005), Roulier et al. (2006)
F	DPM-DFM; 'MACRO-FRAC3Dvs'	1D—distributed MACRO linked with 3D discrete fracture model FRAC3Dvs	Stenemo et al. (2005)
F	DPM; Root Zone Water Quality Model (RZWQM)	1D, Poiseulle, Convection (macropore), Green-Ampt, convection, decay, nonlinear and kinetic adsorption, root uptake (matrix). Hooghoudt drainage, chemical washoff from soil and plant foliage to overland flow.	Kumar et al. (1998), Ghidey et al. (1999), Jaynes and Miller (1999), Wauchope et al. (2004) (review[b]); Malone et al. (2004c,d), Fox et al. (2004, 2006)
F	SPM with bimodal flow scenario; LEACHM	1D, two independent regions (Richards, CDE) with decay, linear sorption.	Elliott et al. (1998)
F	DPM; SIMULAT	1D, Richards, CDE with sorption, decay (matrix); KW gravity film flow and convection (macropores)	Aden and Diekkrüger (2000) (F)
F	MIM, 1D-distributed; MICMAC	1D distributed conceptual model of multiple soil columns with cylindrical macropore located in the center. Monte Carlo simulation.	Bruggeman et al. (1999)
F	SPM; Pesticide Root Zone Model 3.1 (PRZM)	1D, no PF, Monte Carlo stochastic analysis	Carbone et al. (2002)
F	MIM; CRACK-NP	1D, Philip infiltration, Poiseulle flow and convection (cracks), Fickian diffusive transfer (into matrix), Freundlich sorption, first-order decay = f(T,θ)	Armstrong et al. (2000b)
F (L, P)	Model comparison or application reviews: MIM, DPM; e.g. SWAT, MACRO, MACRO_DB, CRACK-NP, SIMULAT, PLM[d]	Various 1D nonequilibrium transport models, questions of inverse parameter estimation and uncertainty	Gottesbüren et al. (2000), Armstrong et al. (2000a), Vanclooster and Boesten (2000) (P); Vanclooster et al. (2000a,b) (L-F); Boesten (2000) (review); Beulke et al. (2001a,b), Dubus et al. (2002a,b) (review), (2003a) (P-F); Garratt et al. (2003), Herbst et al. (2005a,b), Alavi et al. (2007) (P)

Soil Profile (S), Plot (P), Hillslope (H), Field (F); ET—evapotranspiration, T—temperature, PF—preferential flow, K_D—Sorption distribution coefficient, K_s—saturated hydraulic conductivity, θ—soil moisture content, (Yes) means: is considered, but in a simplified way
[a]Synthetic model parameters.
[b]No data.
[c]Combines GLEAMS and DRAINMOD with algorithm for macropore flow.
[d]The following models without PF component are also included: MARTHE, TRACE, ANSWERS, PRZM, LEACHP, WAVE, GLEAMS and PELMO.

consider variable soil cracking as a function of the soil moisture (Ghidey et al., 1999).

Kumar et al. (1998) evaluated the performance of the PF component of RZWQM 3.25 in simulating the effects of the field measured macroporosity on atrazine concentrations in subsurface drain flow from corn fields with no-till and moldboard plow systems. Atrazine concentrations measured in 1990 were used for calibration, and those from 1991 and 1992 were used for model validation. Compared to the RZWQM simulation without macropore flow, using the PF component gave similar results for tile flows, but a strongly improved agreement between simulated and observed atrazine concentrations in both calibration and validation time periods. Simulated atrazine losses were sensitive to lateral mass transfer from the macropores to the matrix, the saturated hydraulic conductivity of the surface layer, and the macroporosity (Kumar et al., 1998).

Malone et al. (2004d) used RZWQM to investigate the effects of hydrology, sorption, degradation and management options (tilled vs. no-till) on observed metribuzin concentrations in percolate, runoff and in the silt loam soil profile of two bare soil field plots (22 m×7 m; 10% slope). The results indicated that (i) the accuracy of the simulated metribuzin degradation rate in the matrix depended on the sorption model used (equilibrium, equilibrium/kinetic, or equilibrium/bound), (ii) the simulated metribuzin degradation rate was apparently slowing down with time due to sorption, and (iii) equilibrium sorption in the matrix was an adequate model despite PF at this site.

Fox et al. (2004) applied RZWQM to study the effects of macropores and subsurface drainage on transport of Br^- and the herbicide isoxaflutole at a 30.4 ha Indiana corn field. After modifying RZWQM to include an 'express fraction' of 2% of the macropores that are in direct hydraulic connection with drains, the model captured the first measured peak in bromide and isoxaflutole concentrations.

3.2.2.2. Deterministic applications of MACRO, a) tracer calibration—pesticide prediction. Larsson and Jarvis (1999) evaluated MACRO 4.1 for simulating the transport behavior of weakly sorbed herbicide bentazone in a silty clay soil plot (0.4 ha) at the artificially drained field site Lanna (SW Sweden). After no-till management for a decade, the soil had numerous cracks and biopores. On-site hourly precipitation measurements were used as the model boundary conditions. Flow and tracer transport parameters in MACRO were manually calibrated using observed water contents, drain water flow, and Br^- concentrations in drain discharge and in the soil profile. The calibration provided acceptable results. Bentazone transport was then predicted using K_{OC} to derive K_D values, assigning a 2% fraction of the sorption sites to the macropore region, and a laboratory measured half life of 12.5 d in the topsoil and essentially infinite in the subsoil. MACRO could predict the bentazone distribution in the soil profile (model efficiency 0.87), while 66% and 89% of simulated concentrations in tile drainage water were within a factor 2 and 5 of the measured values, respectively. Concentration fluctuations in tile outflow were, however, poorly captured. Macropore flow reduced bentazone leaching in this clay soil, because bentazone residing in the matrix was 'protected' against bypass flow in macropores (Larsson and Jarvis, 1999).

Brown et al. (2004) used MACRO 4.1 to model the exposure of agricultural drainage ditches to the herbicide sulfosulfuron in a 7.7-ha field with clay soil in central England. Sulfosulfuron concentrations were monitored in a single drain outlet, and in the receiving ditch 1 km downstream. The total loading to drains was 0.5% of applied pesticide, 99% of which was lost in the first 12.5 mm of drain flow. In the receiving ditch, most concentrations were diluted to below the detection limit. In the application of MACRO, most parameters were derived from measured data mostly using empirical relations given in MACRO_DB (Jarvis et al., 1997). The Freundlich sorption coefficient was derived from a linear relation to pH, independent of the soil organic matter content. Water tension at the boundary between the matrix and macropores was set to values between −2.5 and −3.5 kPa, based on previous applications of MACRO to similar soils (nowadays this value is usually set to −1 kPa, e.g., Jarvis et al., 2007). The amount of pesticide spray intercepted by the canopy crop was set to 79% to match the measured initial soil residues. The MACRO simulation overestimated macropore flow. The peak sulfosulfuron concentrations in drainflow and the total loading to drains were overestimated by factors of 2.4 and 5, respectively (Brown et al., 2004).

Scorza Júnior et al. (2007) tested MACRO 5.1 based on a comprehensive data set obtained at the tile-drained Andelst field site (the Netherlands) with cracking clay soil. In line with EU (FOCUS) procedures, the model was first calibrated against the measured moisture profiles and bromide concentrations in soil and in drain water. The dynamics of the bentazone breakthrough in drain water could then be predicted rather well based on laboratory measurements of sorption and degradation. Predictions of both bentazone and imidacloprid concentrations were within a factor of 3 at worst. This appears to be one of the most accurate predictions, compared to other studies using MACRO (see above), or different models, where uncalibrated prediction often resulted in complete failure (see below, Section 3.2.5). What made this difference, except for using a fairly comprehensive data-set? While further reasons are discussed in section 3.2.5, one aspect of this study was to combine inverse estimation with expert knowledge: the mass transfer coefficient and the kinematic exponent were manually fine-tuned to match those parts of the bromide BTC (initial peak timing and height) thought to be of particular significance for pesticide leaching (Scorza Júnior et al. 2007).

3.2.2.3. Deterministic applications of MACRO, b) inverse analysis and process studies. Larsbo and Jarvis (2005) analyzed data requirements for an inverse identification of input parameters for MACRO 5.0 (Larsbo and Jarvis, 2003). MACRO was applied to model concentrations of Br^- and bentazone measured during one year in a macroporous tile-drained field clay soil (95 by 42 m) at the Lanna site, SW Sweden. Two different calibration and uncertainty estimation methodologies were used: (i) sequential uncertainty fitting (SUFI) (Abbaspour et al., 1997) and (ii) generalized likelihood uncertainty estimation (GLUE) (Beven and Binley, 1992). Six parameters controlling macropore flow, sorption and degradation were determined using inverse modelling and measured Br^- and bentazone concentrations in tile drainage water and in the soil. GLUE required both resident and flux concentrations to obtain highly conditioned and unbiased parameters characterizing pesticide transport. Tracer observations significantly improved the conditioning of macropore flow parameters. Overall, SUFI was assessed to be an efficient parameter estimation tool, whereas GLUE seemed better suited for estimation of uncertainty in predictions (Larsbo and Jarvis, 2005).

Using the simulation for the Lanna site as a base case, Larsson and Jarvis (2000) used MACRO to investigate the effects of compound properties and macropore flow on pesticide leaching for 60 hypothetical compounds with widely differing sorption and degradation characteristics. Sorption and degradation reactions had a similar effect on the vulnerability of pesticide to macropore flow. Macropore flow decreased leaching for mobile and persistent pesticides, while the effects of macropore flow were of little environmental significance for strongly sorbing compounds. Thus, the most pronounced effect of macropore flow was predicted for moderately mobile compounds ($50 < K_{oc} < 5000$ cm^{3}g^{-1}, half-life < 10 days). Reductions in the application dose were suggested to reduce the leaching of such compounds in structured soils. A simple power-law function was proposed to forecast the effect of macropore flow on leaching (Larsson and Jarvis, 2000).

Villholth et al. (2000) modified MACRO to consider particle transport, and to simulate particle-facilitated pesticide leaching. The modified MACRO was calibrated to describe prochloraz transport in a 5-m by 5-m subsurface-drained field plot in Denmark. The plot, which had a macroporous sandy loam soil, was irrigated 3 times during an 8-day period. The drainage flow rate, particulate matter content, and prochloraz concentrations (dissolved and attached to the particulate matter) in the drainage water were monitored. About 0.2% of the applied pesticide mass, 6% of which was associated with the particulate phase, appeared in the drain outflow. MACRO could be calibrated to simulate these observations. Pesticide degradation was less important during this short study time, while sorption was critical. Any discrepancies were attributed to the model's inability to account for kinetic sorption mechanisms to macropore linings and particles (Villholth et al., 2000).

3.2.2.4. Other models. Nicholls et al. (2000) used the Pesticide Leaching Model (PLM 3), as described by Hall (1994) and Nicholls and Hall (1995), to simulate the distributions of Br^-, bentazone and ethoprophos in a sandy soil profile (Vredepeel, Netherlands) and in a cracking clay soil (the Brimstone farm, UK). After an extensive calibration PLM could approximate the drain flow and associated pesticide concentrations at Brimstone, and pesticide distribution profiles at Vredepeel. However, due to the high sensitivity of input parameters that govern macropore flow, the predictive ability of PLM appeared limited (Nicholls et al., 2000).

Jørgensen et al. (2002) used the 3D numerical discrete fracture model FRAC3Dvs 4.0 (Therrien and Sudicky, 1996) to describe vertical pesticide transport through fractured clay-rich water saturated till. The concentrations of Br^-, the mobile compounds mecoprop and metsulfuron and the strongly sorbed prochloraz were monitored in wells of two field plots of 40 m^2 each. Most (96 to 98%) of the vertical water flow took place along root channels within the fractures, while the remaining flow occurred in the clay matrix. Using observed effective fracture spacings and mean fracture apertures as input parameters, FRAC3Dvs approximated measured pesticide concentrations reasonably well (Jørgensen et al., 2002). Jørgensen et al. (2004) further applied FRAC3Dvs to predict the downward migration of mecoprop through a fractured, saturated, clayey till aquitard. The model was first calibrated against laboratory experiments conducted with undisturbed fractured till columns (0.5 m diam., 0.5 m high) and field data of hydraulic heads, fracture spacings, and water budget. Subsequent model predictions suggested that the mecoprop mass flux into the underlying aquifer is largely controlled by pesticide degradation and ground water recharge (Jørgensen et al., 2004).

Kodešová et al. (2005) used HYDRUS-1D with DPM (Šimůnek et al., 1998, 2003) to simulate water movement and chlorotoluron concentrations in the soil profile beneath a 4-m^2 plot. The soil hydraulic properties, sorption distribution coefficient and degradation rate were determined in the laboratory. Simulated chlorotoluron concentrations were overestimated and tended to be higher when using the Freundlich instead of the Langmuir sorption isotherm, even if both isotherms could be fitted equally well to the measured batch sorption data. Assuming degradation in both solid and liquid phases improved the simulation of resident chlorotoluron concentrations (Kodešová et al., 2005). Simulations using a chromatographic single porosity model (SPM) in HYDRUS-1D failed to calculate the chlorotoluron distribution in the soil profile. The DPM significantly improved the correspondence between calculated and observed herbicide concentrations (Kodešová et al., 2005).

Alavi et al. (2007) compared the performance of S1D DUAL (Vogel et al., 2000; Ray et al., 2004) and MACRO 4.3 (Jarvis, 2001) using resident concentration profiles measured for bromide and 5 pesticides in 3 plots with tilled, fine-textured, aggregated tropical soils. Both uncalibrated models gave satisfactory order-of-magnitude predictions of concentration depth profiles. However, there was no evidence of preferential transport (Alavi et al., 2007), which might have been partly attributed to the lack of water and solute flux information.

Elliott et al. (1998) modified LEACHM to simulate preferential displacement of the moderately mobile herbicide clopyralid in an irrigated 4.6-ha tile-drained field site with barley crops under conventional tillage in Saskatchewan, Canada. An estimated 1.6% of the applied clopyralid was lost in the tile drain effluent. LEACHM was used as a pseudo-DPM with independent matrix and preferential flow domains. Surprisingly good agreement between observed and simulated clopyralid concentrations was obtained in both the tile effluent and the soil when 40% of the water was assumed to move through the PF paths characterized using hydraulic conductivities two orders of magnitude larger than for the bulk soil, and the remaining 60% of the water moved through the matrix according to measured hydraulic characteristics. The good performance of the model with independent transport regions led to the hypothesis that lateral transfer may have no net effect on vertical solute fluxes at the field scale (Elliott et al., 1998).

Armstrong et al. (2000b) applied CRACK-NP to model pesticide leaching at the Brimstone farm site (Oxfordshire, UK), characterized by a cracking clay soil. Field observations of the water table, tile drain outflow and isoproturon concentrations in tile effluent of a winter season (approx. daily measurements), and for one selected week (approx. hourly data), were utilized in simulations. Ped sizes, ped sorptivity, macroporosity, and macropore hydraulic conductivity were measured independently. Selected transport parameters were calibrated using measured concentrations of nitrate (assumed to be a conservative tracer) in the tile outflow. The sorption coefficient (K_D) and the half-life of isoproturon were apparently not calibrated, although it was not explicitly stated how they were obtained. The model could predict the drain hydrographs, the timing of the isoproturon main peak, and peak concentrations in the drain occurring with discharge peaks moderately well (Armstrong et al., 2000b).

Aden and Diekkrüger (2000) applied SIMULAT 2.3 (Diekkrüger, 1996) for the modelling of herbicide dynamics at four field sites, including a cracking clay soil (Brimstone, UK) and a macroporous loam soil (Tor Mancina, Italy). Only the soil hydraulic parameters were manually calibrated, while transport and reaction parameters were independently estimated from measurements and literature. For the two sites with the PF paths, SIMULAT could not describe the temporal pattern of drainflow. The isoproturon concentration pattern in the leachate of the Tor Mancina site was not reproduced, although absolute concentrations mostly varied within the measured range. For the Brimstone site, isoproturon concentrations in drainflow were severely underestimated. This was explained as being the result of the lack of coupling between the submodels for macropore and tile drain flow, which forced water into the soil matrix before it could enter the drainage system. Furthermore, using degradation parameters from laboratory incubation studies, SIMULAT underestimated the decay of isoproturon and overestimated the mecoprop degradation in the soil. The laboratory data seemed insufficient for estimating sorption and degradation in the field (Aden and Diekkrüger, 2000).

Difficulties in applying PF models have triggered studies on the calibration of chromatographic models. For example, Scorza Junior and Boesten (2005) investigated whether the CDE-based model PEARL could be calibrated to simulate leaching of Br^-, mobile bentazone, and moderately sorbing imidacloprid observed in drain water and groundwater in a cracking clay soil. A large dispersivity (>60 cm) was calibrated in PEARL, to simulate Br^- concentrations. Bentazone concentrations could then be approximated with PEARL when using a 2.5-times shorter half-life than derived from laboratory studies. The transport of moderately sorbing imidacloprid could not be simulated at all. It was concluded that chromatographic models such as PEARL may sometimes be calibrated to approximate preferential transport of mobile pesticides (Scorza Junior and Boesten, 2005). However in other case studies, CDE-based models could not be calibrated to simulate transport of a tracer during PF (e.g., Gerke and Köhne, 2004). The applicability of chromatographic models will depend on how 'preferential' water flow at a given site is.

In many studies, degradation under field conditions was found to be initially faster than predicted from laboratory incubation tests followed by a slower decay phase (biphasic degradation). Temperatures, water contents, nutrient concentrations and daylight vary in the field and differ from constant lab conditions. The openness of the field system causes various dissipation processes to be lumped into a 'pseudo-degradation'. For instance, while initial rapid losses may occur by volatilization slower dissipation processes, such as photodecomposition on soil and plant surfaces, degradation by adapted microorganisms, leaching and adsorption, or root uptake, may follow, followed by slow biodegradation in the soil. In model applications, as well as in experimental measurements, it is often nearly impossible to properly distinguish between degradation in the soil and other dissipation processes in the field.

3.2.3. Non-localized stochastic applications

Roulier et al. (2006) used MACRO to identify controls on atrazine leaching through luvisols and calcisols overlying fissured limestone at Brevilles, France. The site (100 m × 70 m area) had a large vertical scale (30 m deep). The time scale was also large (36 years). Calibrated MACRO predicted preferential leaching at the base of a 30 m thick limestone sequence within days after heavy rainfall following atrazine application in spring. A Monte-Carlo sensitivity analysis suggested that the degradation rate, sorption and macropore flow in the soil controlled leaching, while variations in the unsaturated rock hydraulic properties were less significant. It was suggested that further study of the sorption and degradation conditions below the root zone would be useful (Roulier et al., 2006).

Stenemo et al. (2005) linked MACRO to the 3D groundwater DFM model FRAC3Dvs in order to simulate pesticide pollution risk of groundwater beneath the fractured till. Mecoprop was monitored in a moraine till and in a local sand aquifer (5 m depth) overlying a regional limestone aquifer (16 m depth) in Denmark. Water and pesticide fluxes calculated by MACRO provided the upper boundary conditions for FRAC3Dvs. While both spatially uniform and variable upper boundary conditions (derived from Monte-Carlo simulations) were used with FRAC3Dvs, they did not show any great effect on simulated mecoprop concentrations in the local sand aquifer. Full connectivity between macropores and fractures across the boundary between the two models was found to be more important. Moreover, the use of effective pesticide fate parameters seemed to be a reasonable practical approach. Furthermore, transient upper boundary conditions resulted into pesticide leaching to the regional aquifer that was 20 times larger than when constant water flow at the same average rate was assumed. The results demonstrated the importance of accounting for transient water flows when modelling deep leaching through fractured porous media to regional groundwater aquifers (Stenemo et al., 2005).

3.2.4. Stochastic distributed approaches

Huang and Hu (2001) and Hu and Huang (2002) developed a stochastic method for predicting contaminant transport through heterogeneous, structured porous media. The mathematically rather intricate approach is built around the DPM of Gerke and van Genuchten (1993) and can consider 3D steady-state PF, linear kinetic sorption and first-order degradation. Hydraulic conductivities, sorption coefficients and degradation rates in the fracture and matrix regions, as well as the inter-region mass diffusion coefficient, were assumed to be random variables. Various correlation functions were assumed to describe the spatial distributions of the parameters. The Euler perturbation method was applied to obtain the analytical solution of mean concentrations in the fracture and matrix regions, which were explicitly expressed by spatial Fourier and temporal Laplace transforms, and which were numerically inverted back to the real space solution via the Fast Fourier Transform method. Exemplary results were shown for 2D reactive transport calculations. The conclusions reveal the complexity of spatial variability effects on the preferential transport of a reactive solute (Hu and Huang, 2002).

3.2.5. Model comparisons at plot and field scales

A common theme of many model comparison studies below is the assessment of model capabilities for an uncalibrated prediction of pesticide transport. This often involved a model calibration stage using hydrological and tracer information, and a predictive model application using laboratory data on pesticide sorption and degradation.

Boesten (2000) reviewed applications and limitations of pesticide behavior models for the soil–plant system, in particular for assessment of leaching to ground water for pesticide registration purposes. The reviewed pesticide leaching models were either chromatographic (based on the CDE) (PELMO, PRZM, GLEAMS, PESTLA, PESTRAS, LEACHP), considered PF (PLM, CRACK, MACRO, SIMULAT), or were of the hybrid type (equilibrium water flow and preferential solute movement) (WAVE and VARLEACH). The following progress was identified: boundary conditions for water flow had become more adaptable, the description of PF in structured soils had improved, linear sorption isotherms had been replaced with Freundlich isotherms, and long-term sorption kinetics had been included in many models. The pesticide degradation submodel was often based on the degradation model PERSIST (Walker and Barnes, 1981), which represents degradation as a first-order rate process that could depend on temperature (Arrhenius function) and soil moisture. PERSIST was evaluated in over 100 studies of pesticide degradation in field topsoils, and performed satisfactorily except for a slight tendency for overestimation. However, according to Boesten (2000), the overall validation status of pesticide leaching models was still low, mostly due to the PF processes, and particularly for small leaching levels of <0.1% of the dose, which are usually relevant for pesticide registration in the EU. Other obstacles to obtaining more reliable model results included the prediction of volatilization fluxes from plant and soil surfaces, and the subjective influence of the individual modeller (Boesten, 2000). Gottesbüren et al. (2000) compared applications of MACRO 3.1/4.0, SIMULAT 2.3, WAVE, LEACHP, and GLEAMS 2.10 by different users for simulating vertical movement of water, Br^-, and isoproturon in a silty loam field soil profile in the Weiherbach catchment, Germany. The field dataset (Schierholz et al., 2000) was split into a calibration stage (1993/1994) and a prediction stage (1995). In SIMULAT, the macropore option was not chosen, because the calibration of bromide transport 1993/1994 in soil was satisfactory using the MIM approach only. The only model which was used with macropore flow was MACRO. The results showed that a good model calibration of Br^- and isoproturon concentrations in one experimental period (1993/1994) did not imply uncalibrated good predictions for the second period (1995), although extensive and detailed laboratory measurements on the pesticide behaviour in the same soil were available. It was not possible to estimate a parameter combination from the laboratory data to describe the field behaviour of isoproturon satisfactorily. Moreover, the dominant influence of individual model users on the modelling results was again striking. Good (MACRO) and fairly good (SIMULAT) isoproturon predictions, respectively, were possible after changing half-lives and sorption coefficients to realistic values as reflected by literature. Furthermore, the authors suggest that comparison of complex models should include evaluating the effects of submodels. For example, simulation results with and without submodels for plant uptake, macropore flow, or temperature effects on degradation, should be compared. This comparison should be followed by a step-by-step validation parallel with defining model parameters, and initial and boundary conditions (Gottesbüren et al., 2000).

Vanclooster et al. (2000a) presented a test of 12 pesticide leaching models applied to four datasets from field and lysimeter studies with unstructured and structured soils, collected in the Netherlands, Germany, Italy and the UK. Model types included those accounting for macropore flow (CRACK-NP, MACRO, PLM), having a simplified description of preferential solute transport (SIMULAT, WAVE), or assuming chromatographic transport (GLEAMS, LEACHP, PELMO, PESTLA, PESTRAS, PRZM-2, VARLEACH). As suggested by Gottesbüren et al. (2000), a stepwise approach was followed to compare submodels simulating the movement of water, solute, heat and pesticide. The experimental dataset was again split into calibration and prediction parts. It was concluded that the predictive capabilities of tested models were still limited due to the lack of information related to macropore flow, pesticide transformation (particularly in subsoil layers), hysteresis in adsorption/desorption isotherms, increase in sorption with time, plant uptake and volatilization (Vanclooster et al., 2000a).

Armstrong et al. (2000a) compared the performance of MACRO, CRACK-NP, SIMULAT and PLM for simulating drainflow and pesticide concentrations in a cracking clay soil at the Brimstone site, UK. PLM was not applicable to a subset of data with an hourly time resolution, since it uses a daily calculation interval. SIMULAT was unable to describe the observed pesticide leaching, reflecting the model's failure to represent the hydrological conditions of the site. Models developed for macroporous soils, CRACK-NP and MACRO, performed better than the more generalized PF models SIMULAT and PLM (Armstrong et al., 2000a).

Beulke et al. (2001a) evaluated the PF models CRACK-NP, MACRO/MACRO_DB, PLM, and SWAT (Brown and Hollis, 1996) for their uncalibrated predictive ability to simulate tile-drain flow rates and associated isoproturon concentrations in a cracking clay soil at the Brimstone site, UK, during three winter seasons. No advantage was found in using mechanistic models (CRACK-NP, MACRO) over simpler models (PLM, SWAT), since no model could consistently predict the data. It was concluded that drainage outflow and pesticide concentrations in drain outflow of structured clay soils under field conditions could not be predicted without model calibration (Beulke et al., 2001a,b).

In contrast, Beulke et al. (1998) conducted a PF model evaluation allowing for some calibration using field and lysimeter datasets from different sites in the UK. For most soils, MACRO either gave results that were similarly good, or outperformed CRACK-NP, PLM, and SWAT. Accordingly, MACRO was the single model recommended for regulatory use. The MACRO_DB system was deemed a useful conceptual development. However, evaluation results suggested that output from MACRO_DB in its (then) present form could not be relied upon for regulatory purposes (Beulke et al., 1998).

Garratt et al. (2003) compared the pesticide leaching models LEACHP, MACRO, PLM, PELMO, PESTLA, PRZM and VARLEACH, and their parameterization, using data involving aclonifen and ethoprophos transport obtained over the course of three years obtained from a 0.3-ha arable field site near Bologna, Italy. Aclonifen is a rather immobile and persistent compound, while ethoprophos is moderately mobile and less persistent. Calibrated and uncalibrated simulations of soil water contents and pesticide concentrations in the soil and ground water were conducted. None of the models could accurately simulate the rapid leaching of pesticide to ground water. The user influence on the parameter selection often played a greater role than the model type in model simulations. Garratt et al. (2003) concluded that the parameterization of macropore flow models needed further improvements. This may include reducing user subjectivity by protocols with methods for determination of each model parameter by measurements, inverse determination (data requirements), or databases. Information about sensitivity and possible ranges of parameters, as depending on the scale and boundary conditions of a model application, would also improve modelling.

Gärdenäs et al. (2006) compared four 2D transport models in HYDRUS-2D (Šimůnek et al., 1999) for predicting PF and the leaching of the herbicide MCPA in a 50-m long transect through a sloping, heterogeneous, tile-drained field soil in South Sweden. The simulated time covered six weeks following the spray application. The 2D approaches included a Richards-CDE chromatographic model with hydraulic properties modified near saturation, a MIM (Richards water flow, mobile and immobile solute transport regions, diffusive mass transfer), a dual-porosity model (mobile and immobile regions for both water flow and solute transport, advective-diffusive mass transfer), and a DPM (two mobile regions). The soil heterogeneity was represented deterministically in 11 different soil zones. Pedotransfer functions derived from the site, lab experiments, literature data and previous field experiments at the site were used to parameterize the flow, transport and reaction processes in the model. The 2D DPM best predicted drainage flow. Only the dual-permeability and dual-porosity models reproduced the pesticide concentration patterns in drain outflow. Furthermore, drains near the hilltop always remained dry, and macropore flow moved laterally through the saturated zone to drains in the midslope and hollow positions (Gärdenäs et al., 2006).

Jarvis et al. (2006) compared simulation results carried out with four CDE-based 1D models (traditional CDE, or CDE plus finger flow, particle-facilitated transport, and kinetic sorption) against imazapyr concentrations observed in 1-m deep soil profiles and groundwater observation wells in the coarse sand and gravel materials of a railway embankment in central Sweden. Only the particle-facilitated transport model (without PF) could reproduce short-term transport observations, but it did not adequately predict imazapyr residues in the soil one year after application. This mismatch suggests that the long-term sorption process, in this case the formation of bound residues, was neglected in all models. The observed much slower degradation of imazapyr after one year supported the notion of 'protected' residues formation (Jarvis et al., 2006).

Fox et al. (2006) compared uncalibrated RZWQM and PRZM predictions against observed Br^- and pesticide concentrations in pore water (from suction samplers), and in the soil at depths down to 210 cm, in two fields in North Carolina and Georgia, USA. Both, RZWQM and PRZM slightly overestimated pesticide displacement through the soil profile. RZWQM generally outperformed or was equivalent to PRZM in simulating concentrations in soil pore water (Fox et al., 2006).

3.3. Scale III (catchment)

Catchment scale pesticide models were developed as tools to quantify the agricultural impact on groundwater quality (Herbst et al., 2005b), to estimate ground water contamination risk and to select high-risk areas for ground water observation networks (Holman et al., 2004; Sinkevich et al., 2005), and to improve the cost-effectiveness of measures needed to achieve the 'good status' of groundwater quality as required, for example, by the European Water Framework Directive (Holman et al., 2004). Until recently, pesticide models at this scale typically did not account for bypass flow and their applications are still rather rare (Table 4). A few different approaches were applied at this scale, including 1D models used with soil and pesticide databases or with stochastic parameter sampling for scenario simulations, 1D distributed modelling, or coupled 1D unsaturated–3D groundwater models. Model validations at scale III face a significant deficit of measurements.

3.3.1. Stochastic applications of 1D models

Lindahl et al. (2005) used MACRO (Jarvis, 1994) with a Monte Carlo technique to analyze the leaching of the herbicide MCPA in the small Vemmenhög catchment (9 km^2) in South Sweden. The authors justified using a 1D approach by pointing to the limited relevance of lateral transport processes (surface runoff, spray drift, groundwater flow) and a rapid drainage routing to the catchment outlet in the Vemmenhög area. MACRO with stochastic parameter sets could predict the hydrologic catchment response, while MCPA concentrations in the stream were mostly underestimated. In particular, the model could not account for high observed concentrations that were apparently caused by the point-source pollution from filling or cleaning spraying equipment (Lindahl et al., 2005). Such farmyard losses may cause short-term high concentration peaks in surface water (Leu et al., 2004), particularly in regions with smaller agricultural fields and a correspondingly larger number of farmyards, such as in SW Germany (Müller et al., 2002).

In a subsequent sensitivity analysis for the Vemmenhög catchment, Lindahl et al. (2005) identified the mass transfer

Table 4
Applications of models simulating preferential pesticide (or reactive solute) transport at scale III

Scale	Model type; name	Dimension, equation name or description	Authors
W (F)	DPM; MACRO—stochastic	Stochastic MACRO simulations parameterized from measured probability distributions	Lindahl et al. (2005)
W	DPM [a] (distributed); Mike She/Daisy+MACRO	Groundwater: 3D Darcy, surface: 2D overland flow, 1D channels, vadose zone (MACRO): Richards, CDE (matrix); kinematic wave, advection (macropores), sorption	Christiansen et al. (2004)
W	DPM; MACRO+spatializing tool	1D—distributed MACRO, GIS compatible	Esposito et al. (2005)
W	SPM; TRACE (flow), SUCROS (plant), 3DLEWASTE (transport)	3D (Richards, CDE) with nonlinear sorption	Herbst et al. (2005a,b)
W	DPM; Generalized Preferential Flow Model and GIS	1D distributed, steady-state flow. Transmission zone: CDE in PF paths (no matrix), distribution zone: exponential loss due to leaching and biodegradation.	Sinkevich et al. (2005)
W [b]	DPM; MACRO Emulator coupled with AQUAT System	Tabular database of over 4000 MACRO scenario simulations are used by AQUAT to predict maximum annual concentrations reaching groundwater surface below the base of the soil profile.	Holman et al. (2004)

Watershed (W), Field (F).
[a] Synthetic model parameters.
[b] National scale of Great Britain.

coefficient as the most influential variable, as opposed to studies at smaller spatial and temporal scales that found degradation, sorption, and—when PF was involved—hydraulic parameters to be the most influential parameters for pesticide transport (e.g., Roulier and Jarvis, 2003a,b). The variation in precipitation during the 2.5 weeks following application and the organic carbon content were the other sensitive variables, whereas the small measured variability in the herbicide degradation rate had little effect on MCPA losses (Lindahl et al., 2005).

Brown et al. (2004) used MACRO to predict the long-term fate of the herbicide sulfosulfuron in 20 environmental scenarios devised for the target area of wheat-growing land in England and Wales (1.7×10^6 ha). The scenarios comprised discrete classes of the soil type and climate, using the SEISMIC database (Hallet et al., 1995). The sulfosulfuron concentrations in a receiving ditch estimated using MACRO were weighted according to the likelihood of each scenario to produce a probability distribution of daily exposure (Brown et al., 2004).

3.3.2. Spatially distributed model applications

Holman et al. (2004) developed a model system for predicting large-scale pesticide losses to groundwater through the matrix and macropores. The 1D distributed model system was based on MACRO 4.1 for the top 1 m of soil profile, and the attenuation factor leaching model AQUAT (Hollis, 1991) for the deeper part of the soil profile. The objective was to develop a diffuse source groundwater contamination calculator for the Prediction of Pesticide Pollution in the Environment (POPPIE) system, which is used by the Environment Agency of England and Wales for driving and refining pesticide monitoring programs (Brown et al., 2002). A fast MACRO emulator was created that uses look-up tables based on the results of 4704 MACRO simulations of pesticide leaching scenarios for different soils, pesticide half-lives and K_{OC} values, weather (excess winter rainfall) and application seasons (spring or fall). The MACRO emulator could predict pesticide losses from 12 combinations of lysimeters and pesticides in a qualitative sense ('leaching or not') with actual concentrations reproduced within an order of magnitude. The linked MACRO emulator/AQUAT system was applied for the entirety of England and Wales at a spatial resolution of 2×2 km. When tested against national monitoring data for pesticides in UK aquifers, realistic regional leaching patterns of atrazine, isoproturon, chlorotoluron and lindane were predicted (Holman et al., 2004).

Esposito et al. (2005) developed a distributed approach to modelling pesticide leaching on the catchment scale using MACRO. Their tool assembles input data for MACRO in a grid, runs MACRO for each grid cell, and creates output files for GIS or other environmental software. Thus, the tool may be used as an interface between MACRO and regional 3D ground water models. It was successfully tested to simulate isoproturon fate during 10 years in the Zwischenscholle test area (20 km^2), Germany, which is characterized by intense agricultural use and shallow groundwater (Esposito et al., 2005).

Christiansen et al. (2004) extended the MIKE SHE/Daisy code with a macropore flow description derived from MACRO. They described spatially distributed pesticide transport in a small part (1.5 km^2) of a catchment in Denmark. The model was applied in a telescopic approach (1.5 km^2, 13.7 km^2, 62.3 km^2) to account for lateral groundwater exchange. A large spatial variation of macropore flow was found, due to the variability in topography and depth to the groundwater table. Simulation results suggested a significant effect of macropores on pesticide leaching to groundwater at the catchment scale (Christiansen et al., 2004).

Herbst et al. (2005b) developed and applied an integrated modelling approach of pesticide transport. The 3D numerical model TRACE (Vereecken et al., 1994), based on the Richards equation, was linked with 3DLEWASTE (Yeh et al., 1992) that solves the CDE, and with a plant module. The resulting model accounts for spatial heterogeneity, though not explicitly for PF. Isoproturon transport in the 20-km^2 Zwischenscholle area (Germany) was described for a 10-year period. The 3D model domain comprised 20,000 nodes and had a horizontal grid size of 200 m, vertical intervals ranging from 1 cm (top) to 10 cm (bottom of the profile) for the soil profile and variable thicknesses for the aquifer grid cells. Parameters were derived from measurements, pedotransfer functions and literature. Measured piezometric heads were reproduced by model results. Relatively high isoproturon concentrations in groundwater were predicted for locations with thin layered and permeable soils (Herbst et al., 2005b).

Sinkevich et al. (2005) developed and tested a GIS-based risk assessment model for ground water contamination by pesticides. The Generalized Preferential Flow Model by Kim et al. (2005) was implemented in a GIS framework. In the topsoil layer, an exponential loss was assumed due to leaching and biodegradation, while in the subsoil transmission zone, solute transport via steady-state PF is calculated utilizing analytical solutions of the CDE. The model system uses land cover data and information about chemical properties and ground water recharge to estimate the chemical concentration reaching the ground water. The distributed risk assessment tool was tested by comparing the model-predicted risk with observed atrazine and nitrate concentrations from 40 sampling wells in Cortland County, New York, USA. Nitrate was considered as an indicator of agricultural pollution. The predictions agreed well with observed nitrate concentrations and pesticide detections and suggested that the high-risk areas constituted only 5% of the catchment. Focusing ground water monitoring in only these areas would be more effective than implementing an evenly distributed country-wide program (Sinkevich et al., 2005).

4. Comparing model strengths and weaknesses

A number of models have been developed, tested, and applied that consider the effect of variably-saturated, transient PF on transport of agrochemicals, such as pesticides. Most models included in this review are 1D approaches based on the two- (or three-) region concept (e.g. RZWQM, MACRO, HYDRUS-1D, CRACK-NP, SIMULAT, PLM, S1D DUAL, SWAT). Model comparisons have demonstrated that all of the above models are clearly superior to chromatographic models in their ability to simulate pesticide displacement in structured soils. With regard to their PF description, the models differ in their philosophy, complexity, and equations used for (i) displacement of water and tracer in and between the domains (see companion paper), and (ii) sorption and degradation in the domains. The first part of the list (i) indicates the prevalent type of the soil structure targeted by the models;

cracked clay soils: CRACK-NP, MACRO; soils with large continuous macropores: RZWQM, MACRO, and soils with hierarchical structure: HYDRUS-1D, S1D DUAL, SIMULAT.

It is not possible to identify a particular PF-pesticide-transport model that is clearly superior for all purposes. Having more model comparisons using benchmark data sets would be useful to compare the calibrated or uncalibrated model performance for different pesticides (including water flow and tracer transport), for different soils, and agricultural management practices. However, three model systems, i.e., MACRO, RZWQM, and the HYDRUS-1D/-2D/(2D/3D) model set, appear to stand out regarding their (i) ease-of-use: graphical (Windows) user interfaces, pedotransfer functions, inverse parameter estimation procedures, and detailed documentation, (ii) complexity: physics-based processes and options (Table 1), boundary conditions, (iii) up-to-dateness: continued upgrades, availability, and support (e.g., discussion forums), and (iv) distribution: large number of published applications.

The RZWQM model (e.g., Ahuja et al., 2000a,b) was developed within the US Department of Agriculture, Agricultural Research Service (USDA-ARS), and was applied particularly in the USA. As an agricultural systems model, RZWQM exceeds the other two models, and maybe any other model, in its options for considering agricultural management including tillage and schemes for crop rotation, irrigation, fertilizer, pesticide and manure applications. Furthermore, it can be used to estimate crop yield and herbicide transport in surface runoff (Malone et al., 2004a; Ma et al., 2007). Different submodels are included to describe equilibrium and kinetic sorption of pesticide in the sil matrix. However, by comparison with the MACRO and HYDRUS models, the description of preferential solute transport in the matrix and macropores and of lateral transfer is more empirical. Examples thereof are the assumed exponential decrease of concentrations in macropores with depth and the assumptions of one way (macropore-to-matrix) water transfer, and of instant partial solute mixing, between both domains. Sorption and degradation are not considered in the macropore region, which is a 'worst-case' assumption. Experimental and modelling evidence showed that despite of limited contact time and contact area, sorption affected preferential pesticide leaching (e.g., Jørgensen et al., 1998; Malone et al., 2001; Rahman et al., 2004) within the PF domain (e.g. Mallawatantri et al., 1996; Stehouwer et al., 1994). This semi-empiricism in the description of PF related processes may not be critical for site-specific calibration, but might potentially limit the development of methods to estimate RZWQM soil hydraulic and transport parameters from soil properties. Finally, RZWQM was linked with GIS for catchment modelling (Wang and Cui, 2004; Ascough et al., 2005).

MACRO (Jarvis, 1994) was often applied, particularly in Europe, to simulate pesticide transport in agricultural soils. For example, MACRO has been coupled to one of the European scenarios to estimate leaching of pesticides to ground water for regulatory purposes (FOCUS, 2000). Compared with the RZWQM, the descriptions of flow, transport, bi-directional lateral transfer, and sorption and degradation in both the matrix and macropores permit a more flexible and physically based description of preferential flow effects on pesticide transport. Reverse (matrix-to-macropore) solute transfer in its advective part proceeds instantaneously for excess matrix saturation. This is not necessarily a realistic concept (Köhne et al., 2004), but has no effect when reverse solute transfer proceeds by diffusion. Since both RZWQM and MACRO assume gravity-driven flow in the macropores, the preferential flow component cannot easily be generalized to two or three dimensions. However, the concepts in MACRO were included in the 2D/1D (matrix-macropores) M-2D model (Kohler et al., 2001). MACRO was also coupled with other models for regional scale applications (section 3.3.).

HYDRUS-1D (Šimůnek et al., 1998, 2003, 2005, 2008a, 2008b; Šimůnek and van Genuchten, 2008) has been used in numerous applications worldwide. However, despite of recent extensions of its PF options (Šimůnek et al., 2003; Šimůnek and van Genuchten, 2008), the model has not yet been tested as often as RZWQM and MACRO for describing pesticide transport experiments. Among the models in this review, HYDRUS contains the most wide-ranging options regarding (two-domain) boundary conditions, flow-transport concepts (one to three domains), degradation and sorption in the soil (including kinetic sorption and degradation in different soil pore systems), transport of metabolites, and particle transport. The more often applied HYDRUS-1D submodels consider the Richards equation and CDE also for the PF system, instead of gravity-driven flow and convection as considered in RZWQM and MACRO. A HYDRUS-1D variant was developed to describe gravity-driven flow and convection (Novák et al., 2000). The Richards-CDE submodel is conceptually better suited to loamy soils, than to heavy clay soils with shrinkage cracks (see companion paper for a discussion). The two or three dimensional versions HYDRUS-2D (2D/3D) (Šimůnek et al., 1999, 2006b) additionally provide tools for representing soil heterogeneity and can consider preferential transport in different directions.

All three models contain some provisions for estimating parameters from basic data. However, even the most ambitious database, the MACRO_DB (Jarvis et al., 1997) system for the selection of soil hydraulic and crop parameters, still needs improvement before it can be recommended for regulatory use (Beulke et al., 1998). Further research in that direction has shown promise (Jarvis et al., 2007). By comparison, the other three models shown in Table 1 (SIMULAT, PLM and CRACK-NP) are less comprehensive, more empirical, and have not been applied as often. SIMULAT does not consider sorption and degradation in macropores, nor volatilization and plant solute uptake. PLM does not simulate a ground water table, and is empirical in its capacity description of water flow with a calculation time interval of 1 day. However, in applications where model parameters are unknown, the more physically based models were not always superior.

One also needs to keep in mind that not all soils show macropore flow and preferential pesticide leaching: as just two out of many examples not reviewed here, both successful application of RZWQM without macropore option (Jaynes and Miller, 1999) and of the Pesticide Root Zone Model (PRZM), which does not consider PF (e.g., Carbone et al., 2002), were reported. PRZM-3 is used by the United States Environmental Protection Agency (US EPA) for Tier II screening of pesticide leaching into groundwater, even though it does not consider PF.

5. Conclusions: progress, problems, outlook

The fate and transport of pesticides in structured field soils is often affected by PF. Considerable progress in modelling pesticide transport under such conditions has been achieved in the past decade using two- (or three-) region models (e.g. RZWQM, MACRO, HYDRUS-1D, CRACK-NP, SIMULAT, PLM, S1D DUAL, SWAT). Scientific progress in model development comprises descriptions of domain-separated equilibrium and/or kinetic sorption and degradation for variably-saturated flow conditions, and other surface and subsurface processes. More practical aspects of progress in the model applicability include development of graphical user interfaces, provisions for inverse parameter and uncertainty estimation, continued availability, upgrading and support, documented tests and applications. When all above aspects are taken together, MACRO, HYDRUS-1D, and RZWQM are the leading model systems for simulating preferential pesticide transport in agricultural structured field soils.

Progress in utilizing inverse and uncertainty parameter estimation techniques for simulating preferential pesticide transport can yield suggestions for future research (see below). For uncalibrated modelling of preferential pesticide transport, using a model calibrated to water and tracer observations and laboratory sorption and degradation data, a satisfactory prediction of concentrations within a factor 3–5 of the measured concentrations was reported in a few cases usually involving MACRO. More often, particularly for blind validation, deviations between observed and predicted concentrations of one or several orders of magnitude were found. Identifying conditions for successful predictions could also give some guidance for future applications (see below). Improvements in the applicability of PF pesticide models proceed through an iterative process between experiments and model evaluations. Measurement techniques need to be improved for deriving PF-transport parameters. Model process descriptions need to be further enhanced. On the other hand, since model complexity cannot increase *ad infinitum*, options to use simplified descriptions should be also identified for certain settings. Based on the model application studies reviewed here, the following needs in PF pesticide modelling and in further research are proposed.

5.1. Improving predictive model capabilities

1) Any research experiment should, as far as possible, have a closed pesticide mass balance (of the parent compound and its metabolites) by including time-series of flux concentrations, final soil resident concentration profile, losses via plant-uptake and volatilization. The use of tracer and compounds of different mobility would be helpful. 2) On the soil column scale, development of PF-related pedotransfer functions, e.g., for the mass transfer coefficient, based on basic soil properties is needed. 3) The preceding approach will have limitations, so additionally, computer tomography should be combined with hydraulic and solute transport measurements to identify characteristic 'form-and-function' relations between the soil structure and flow-transport response. 4) Degradation and sorption in the macropores and soil matrix should be distinguished, e.g. by *in-situ* measurements of degradation in earth-worm burrows (tedious) or lab measurements of sorption and degradation using the soil material sampled from the matrix or PF paths material. Techniques for identifying the relation between soil structure, their biochemical characteristics, and resulting sorption or degradation functions should be developed; organic tracers might play a role in this effort. 5) On a soil profile scale, the 'form–pattern–function' relation should be established, between 'form' (structure: layers, layer interfaces, heterogeneity, macropores), 'transport patterns' (PF network formation, lateral redistribution, dispersion), and functional descriptions of this relation. Promising approaches are the 'scaleway' (Vogel and Roth, 2003) or classification of transport patterns in soil horizon sequences (Kulli et al., 2003). 7) On a field scale, the effect of spatial variation of hydraulic, sorption and degradation properties (in macropores and matrix) can be considered by uncertainty estimation. 8) Seasonal variability of the agricultural soil–plant system, and the short-term variability of rain intensity, need to be considered in adequate time resolutions. 9) Both physical and chemical nonequilibrium should be considered in PF and matrix domains, as e.g. done in HYDRUS-1D. 10) Particle facilitated transport for strongly sorbing pesticides could be added. 11) Further model comparisons (including DFM approaches) exploring the capability and importance of individual model subcomponents should be performed based on benchmark data sets. 12) Closely related, the relative importance of different processes (PF, leaching, sorption on plant residues and in soil, volatilization, overland flow) for the overall pesticide loss from the field should be further compared. 13) Calibrated parameter values and their ranges, improved pedotransfer functions, and other information facilitating parameter determination, should be assembled in meta-databases for different structured soil types, crops, and agricultural management. Some of these issues will be addressed in a European collaborative research project named 'footprint' (http://www.eu-footprint.org/ataglance.html–Sep 2008).

5.2. Improving calibrated model capabilities

This includes the above efforts for reducing model errors by improving process descriptions, and furthermore requires improved inverse procedures and data. 1) Inverse parameter estimation should simultaneously use all data (not sequentially use water, tracer, and pesticide data). Proper identification requires flux and resident concentrations and probably some domain-specific information on sorption and degradation. Standard batch or incubation techniques are usually not representative of in-situ unsaturated matrix conditions, even if they (by volume) approximately represent the matrix. 2) Parameter sensitivities: many studies have analyzed parameter sensitivity. Results could be used to systematize model parameter sensitivity as depending on few structured soil categories, compounds (mobile versus strongly sorbed), and length and time scales (e.g., a 2-wk column study versus a 2-yr lysimeter experiment). 3) In order to reduce the effect of user subjectivity, 'correct' example simulations and/or a protocol with rules for model setup for different scales and settings should be included with the model code. 4) Model calibration preceding model validation should focus on matching those parts of the tracer data (usually time and peak of initial tracer breakthrough) that contain the most PNE information for pesticide breakthrough. Advanced corresponding weighting schemes could be developed in automated inverse procedures.

Moreover, there are indications of a significant effect of macropores on pesticide leaching to groundwater at the catchment scale. At this scale, 1D models used with soil and pesticide databases or with stochastic parameter sampling, 1D distributed modelling, or coupled 1D unsaturated–3D groundwater models were used. However, model applications at this scale faced a significant deficit of measurements and appear to be in an early research stage.

Generally, the model analysis of preferential pesticide leaching has made significant progress in the past decade and will undoubtedly be developed further. By assessing the safety of new compounds in the regulatory process, or identifying hot spots of high groundwater vulnerability that would require reductions in pesticide dose or use of organically grown crops, such model applications can assist in reducing the environmental (and economic) impact of pesticide applications on water resources.

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